

**DOCUMENTATION OF THE SAPRC99  
CHEMICAL MECHANISM FOR  
VOC REACTIVITY ASSESSMENT**

INCOMPLETE DRAFT

**FOR REVIEW PURPOSES ONLY  
NOT FOR ATTRIBUTION**

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By

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## II. CHEMICAL MECHANISM COMPONENTS

The major components of the SAPRC mechanisms are the base mechanism, the mechanism and parameters for the detailed model species, and the lumping procedures. The base mechanism is the portion of the mechanism used to represent the reactions of the inorganic species, the common organic products, the intermediate radicals leading to these products, including those formed from the initial reactions of the detailed model species. The detailed model species are used to represent most of the emitted VOCs, which are not in the base mechanism. These can be added to the mechanism (either as explicit reactions for individual VOCs or as lumped model species whose parameters are derived from the mixture of detailed model species they represent), as needed in the model application. The detailed model species include those that have explicit rate constant and product yield parameters assigned for all their relevant atmospheric reactions, and those, which are represented by other model species using “lumped molecule” assignments.

In this section we discuss the components of the mechanism that are derived from chemical mechanistic considerations. This includes the base mechanism and those detailed model species for which kinetic and mechanistic parameters have been derived. The evaluation of these components of the mechanism against environmental chamber data is then discussed in the following section. After that, the lumping procedures used to represent complex mixtures, and other considerations involved when implementing this mechanism in airshed calculations are discussed.

### A. Base Mechanism

The base mechanism is the portion of the mechanism which must be incorporated when representing the reactions of any generic VOC, and includes the inorganic reactions, the reactions of the common organic products and the reactions of the common radicals formed from these products or any generic VOC. A complete listing of the base mechanism is given in Appendix A on Table 45 through Table 48. The species used in the base mechanism listed on Table 45, their reactions and rate constants listed on Table 46, the rate constant and mechanism documentation notes referred to there are given in Table 47, and the absorption cross sections and quantum yields for the photolysis reactions listed on Table 48. The major features of the mechanisms, and the changes made relative to the previous version (Carter et al, 1997a) are discussed in the following sections.

#### 1. Inorganic Reactions

The inorganic reactions in the mechanism are essentially the same as in the previous versions, except all the rate constants have been updated based on the results of the most recent evaluations (Atkinson et al, 1997a,b, 1999; Atkinson, 1997a; NASA, 1997). This resulted in changes to most of the rate constants, though in most cases the changes were small probably not of significance to model predictions. In addition, a few reactions that were previously judged to be negligible were added to extend the range of validity of the mechanism. The changes that may not be negligible, and the aspects of the inorganic mechanism that are still considered to be uncertain, are briefly summarized below, in the order that the reactions appear on Table 46.

- Reactions of  $\text{O}^3\text{P}$  with  $\text{O}_3$  and  $\text{NO}$ , which were omitted from the previous mechanism, are now included. These are believed to be negligible under most atmospheric conditions, but may not be in some high concentration experiments.



- The rate constant used for the “homogeneous” portion of the  $\text{N}_2\text{O}_5$  hydrolysis reaction was decreased from  $1 \times 10^{-21} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  to  $2.6 \times 10^{-22} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , based on the data of Mentel et al (1996). Note that this reaction may be primarily heterogeneous in nature, and the appropriate rate constant to use in atmospheric simulations is uncertain. However, the rate constant we use is not inconsistent with the IUPAC (Atkinson et al, 1997b) recommendation that the gas-phase rate constant is less than  $2 \times 10^{-21} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ .
- The rate constant for  $\text{OH} + \text{NO}$  for 1 atmosphere and 300K increased by over a factor of 1.5, based on the NASA (1997) recommendation for the high pressure rate constant. The IUPAC (Atkinson et al, 1997a) recommendation is to use an even higher high pressure rate constant, but that recommendation is not used because the NASA value is more consistent with measurements made under near-atmospheric conditions.
- There is a significant discrepancy between the NASA (1997) and IUPAC (Atkinson et al, 1997a) recommendation concerning the important  $\text{OH} + \text{NO}_2$  reaction. Again, the NASA recommendation is preferred because it is more consistent with measurements made under near-atmospheric conditions. [The rate parameters actually used are those that will be in the update to the NASA (1977) evaluation (Golden, private communication, 1999).] The high  $k_\infty$  recommended by IUPAC is based on very high pressure data in helium, and may be artifacts due to the contribution of a second reaction channel, involving  $\text{HOONO}$  formation, becoming important at higher pressures (Golden, personal communication, 1998). The value used in the current mechanism is about 20% lower than that used in the previous version. Given the importance of this reaction as a radical termination and  $\text{NO}_x$  removal process, this change may have a non-negligible effect on model simulations.
- The reaction of  $\text{OH}$  with  $\text{HONO}$ , which was omitted in the previous mechanism because of its low importance in ambient simulations, is now included. This reaction can be important in simulations of experiments with  $\text{HONO}$  added as a radical source, which may be useful for assessing some aspects of VOC reactivity (unpublished results from this laboratory).
- A second photolysis channel for  $\text{HONO}$ , forming  $\text{H} + \text{NO}_2$ , was added based on the IUPAC (Atkinson et al, 1997) recommendations. This channel is calculated to occur ~10% of the time under atmospheric conditions.
- The reaction of  $\text{OH}$  with  $\text{NO}_3$ , omitted from the previous mechanism, is now included. The possibility that it may be non-negligible under some nighttime conditions or in some dark experiments has not been ruled out.
- The rate constant for the reaction of  $\text{HO}_2$  with  $\text{NO}_3$  was increased based on recent laboratory data of Mellouki et al (1993).
- The reaction of  $\text{NO}_3$  with itself, which may be non-negligible under some nighttime conditions (Stockwell et al, 1997) is now included.

The effects of these changes on model simulations have not been evaluated. It is expected the ~20% change in the  $\text{OH} + \text{NO}_2$  may be the most important in terms of predictions of ozone formation, and in the model simulations of the environmental chamber experiments used to evaluate the mechanism, as discussed in Section III. However some of the changes concerning  $\text{NO}_3$  reactions may have non-negligible effects on nighttime simulations. As indicated above, a number of changes were added that are not expected to influence ambient simulations, but which may be important in simulations of experiments that may be useful for evaluating other aspects of the mechanism. Since including these reactions did not add new species to the model, the impact of these reactions in terms of computational burden in airshed models should be minor.

## 2. Representation of Radical Species

The approaches used to represent the various types of radical species formed in the atmosphere are discussed in this section. As with the previous mechanism, most of the inorganic and a few of the organic radicals are represented explicitly, but most of the organic radicals are either lumped or not explicitly represented in the model. In particular, rapidly-reacting organic radicals which either react in only one way or whose reactions do not depend on other reacting species are replaced by the set of products they form, and most other radicals are either lumped or represented using a limited number of chemical “operators”. The various approaches employed are discussed in this section.

With regard to computational impacts of radical species incorporated in the model, a distinction is made between *active* species and species where the *steady state* approximation can be employed. Active species are model species whose concentrations need to be calculated by the solver software by integrating their rates of change, and which must be transported in multi-cell model simulations. Steady state species are model species (usually representing rapidly reacting radical or chemical operators representing radicals) for which the steady state approximation can be employed. In that approximation, the concentration of the species is calculated at each time step assuming that the instantaneous rate of formation is equal to the rate of destruction. This means that the species does not need to be transported or integrated by the model software, saving computer time and memory in multi-cell simulations. This approximation can appropriately be used by species such as alkyl and alkoxy radicals that always react rapidly with  $O_2$  or have rapid unimolecular reactions, and is implicitly used when a radical is removed in the model by replacing it with the compound(s) it forms. However, experience has shown that it cannot be used for peroxy or  $NO_3$  radicals, since their loss processes can become slow compared to their rates of change under low  $NO_x$  conditions or at nighttime. In addition because of limitations in the mechanism compiling software used in this work [and also implemented in the FCM version of the UAM (Kumar et al, 1995) and the CALGRID model (??)], the steady state approximation cannot be used for species that react with themselves, other steady state species, or whose instantaneous concentrations cannot be calculated from the active species concentrations in a stepwise manner (Carter, 1988). Because of the latter restriction, the steady state approximation cannot be used for OH radicals when the mechanism is implemented with this software, though probably it is not a bad approximation for this species.

### a. Inorganic Radicals

Most of the inorganic radicals in the mechanism are represented explicitly, as shown on Table 45. The two exceptions are H atoms and  $HOSO_2$  radicals, where the latter is formed in the reaction of OH with  $SO_2$ . H atoms are assumed to react exclusively and rapidly with  $O_2$  to form  $HO_2$ , so any reaction that forms H atoms is represented as forming  $HO_2$  instead. Likewise,  $HOSO_2$  are assumed to react primarily with  $O_2$  to form  $HO_2$  and  $SO_3$ , so it is replaced by the  $HO_2$  and sulfate (SULF) model species in the OH +  $SO_2$  reaction. Table 45 indicates those radicals for which the steady state approximation can be used. Note that this approximation should not be used for  $HO_2$  or  $NO_3$  radicals because they may build up significantly in concentration at nighttime or in the absence of  $NO_x$ . It probably could be used for OH radicals, but is not because of limitations of software used to implement the mechanism, as indicated above.

### b. Rapidly Reacting Radicals.

As with the previous versions of the mechanism, many rapidly radicals are removed from the mechanism by replacing them by the species they are assumed to rapidly form. Note that this can only be done for radicals where (1) the steady state approximation is appropriate, (2) the product(s) they ultimately form do not depend on any other reactants, and (3) the products they form also do not depend

on reaction conditions (e.g., temperature) or the variation can be assumed to be insignificant for the conditions of the model application. The specific types of rapidly reacting radical substitution reactions used in this mechanism are as follows. Except as indicated, the substitution is due to an expected rapid reaction of the radical with  $O_2$ .

- HCO is replaced by  $HO_2 + CO$ .
- Based on product data for reactions of OH radicals with alcohols and other species,  $\alpha$ -Hydroxy alkyl radicals are assumed to react with  $O_2$  primarily by abstraction from the  $\alpha$ -hydroxy rather than by addition. Therefore, such radicals are replaced by  $HO_2$  + the corresponding carbonyl compound formed when it reacts with  $O_2$ . For example,  $CH_3CH(\cdot)OH$  is replaced by  $CCHO + HO_2$ , where CCHO is the model species for acetaldehyde.
- $\alpha$ -Nitrato alkyl radicals are assumed to decompose unimolecularly to  $NO_2$  + the corresponding carbonyl compound sufficiently rapidly that the decomposition will dominate over reaction with  $O_2$ . Therefore, such radicals are replaced by  $NO_2$  + the corresponding carbonyl compound formed in the decomposition. For example,  $CH_3CH(\cdot)NO_2$  is replaced by  $CCHO + NO_2$ .
- All other carbon-centered radicals, including acyl ( $RCO\cdot$ ) and alkyl ( $R\cdot$ ) are assumed to react entirely by  $O_2$  addition. Therefore, these are replaced by the corresponding peroxy radical whenever they are formed.
- With the exception of t-butoxy (model species TBU-O $\cdot$ ) and phenoxy (model species BZ-O $\cdot$ ) radicals, which are represented explicitly in the mechanism, all alkoxy radicals are replaced by the set of products they are assumed to form when they react under atmospheric conditions. This would include reactions with  $O_2$  and/or unimolecular reactions, as applicable. If the alkoxy radical has more than one reaction pathway that is assumed to be non-negligible, then non-integer stoichiometric coefficients are used for the products, as appropriate. The reactions of alkoxy radicals are discussed in Section II.B.10.
- The Crigiee biradicals formed in the reactions of  $O_3$  with alkenes are replaced by the set of products they are assumed to form when they react in the atmosphere, which includes stabilization as well as the various decomposition pathways. These reactions are probably temperature and pressure dependent, but since insufficient information is available to estimate these dependences, this is ignored. The reactions of Crigiee biradicals are discussed in the Section ??, in conjunction with the discussion of the general methods used for estimating  $O_3$  + alkene reaction mechanisms.
- Stabilized Crigiee biradicals are replaced by the corresponding organic acid, on the assumption that their major fate under atmospheric conditions is reaction with  $H_2O$  to form the acid. The assumption that reaction with  $H_2O$  is the major fate of the biradicals is consistent with the rate constant ratios cited by Atkinson (1997a) for the reactions of  $HCHO_2$  with  $H_2O$ ,  $HCHO$ ,  $CO$ , and  $NO_2$ . The mechanism for the reactions of stabilized  $HCHO_2$  with water appear to be complex and may involve some formation of  $H_2O_2$  or other peroxides, but based on the discussion of Atkinson (1999) we assume that acid formation is the major fate of all the stabilized Crigiee biradicals.

Note that branching ratios for some of the alkoxy radicals and the Crigiee biradicals may be temperature and pressure dependent, and this treatment ignores these dependencies. As discussed in Section II.B.10, the alkoxy radical branching ratios are estimated for 300°C and 1 atmosphere total pressure, and thus they may not be optimum for simulations of high altitude or extreme temperature conditions. However, it should be pointed out that no other current mechanism represents these temperature and pressure dependences of product branching ratios, and doing so would require a significant increase in the complexity of the mechanism, or would require the model software to support temperature and pressure-varying parameters. Since no information is available concerning the temperature and pressure dependences of Crigiee biradical reactions, any representation of this in the model would be entirely speculative.

### c. Explicitly Represented Organic Radicals

Most of the organic radical species are represented either by replacing them with the radicals or products they are expected to exclusively form, or by using the lumped peroxy radical species or “operators” as discussed in the following two sections. However, a few organic radical species are represented explicitly, either because their reactions are sufficiently different that they are not appropriately represented using the other approaches, or because it is believed representing them explicitly will improve the accuracy of the model sufficiently to make the added model species worthwhile. These are briefly discussed below.

Methyl Peroxy Radicals. In the previous mechanism, all peroxy radicals, including methyl peroxy, were represented using the general peroxy radical operators + the products they were expected to form, as discussed below. In this approach, the same organic products are assumed to be ultimately formed regardless of whether the radical reacts with NO, HO<sub>2</sub>, or another peroxy radical. Although as discussed below this approach is still used for most of the higher peroxy radicals in this mechanism, in this mechanism methyl peroxy radicals (CH<sub>3</sub>OO·) are represented explicitly, using the model species C-O2·. Thus, the appropriate C<sub>1</sub> products are formed when it reacts with HO<sub>2</sub>, itself, or other peroxy radicals, which are different than the formaldehyde formed when it reacts with NO. This allows for a more accurate representation of the reactions of at least this peroxy radical and gives this mechanism a level of detail approaching that of the RADM2 (Stockwell et al, 1990) or RACM (Stockwell et al, 1997) mechanisms in the way peroxy radical reactions are treated. As discussed by Carter and Lurmann (1990), the peroxy radical lumping approach used in the RADM2 mechanism appears to be somewhat less approximate than the lumping approach used in the previous SAPRC mechanisms.

Note that the reactions of peroxy radicals with NO<sub>3</sub> were not in the previous version of the mechanism. This reaction, which may be non-negligible at nighttime, was added based on the recommendations of the current evaluations (Atkinson et al, 1997a,b).

Acyl Peroxy Radicals. The previous mechanism used separate steady-state model species to represent acyl peroxy radicals (CCO-O2·), general lumped higher acyl peroxy radicals (C2CO-O2·), and the higher peroxy radicals formed from glyoxal (HCOCO-O2·) and benzaldehyde (BZCO-O2·). In addition, the model species (RCO3·) was used to compute the total concentration without using the steady state approximation, for the purpose of computing peroxy + peroxy reaction rates. The PAN analogues for these radicals (PAN, PPN, GPAN, and BZ-PAN) were also included in the mechanism as active species. In this mechanism, the acyl peroxy radical formed from glyoxal (and its PAN analogue) are removed by lumping them with the other higher general lumped peroxy radicals (or PAN analogues), the acyl peroxy radical (and PAN analogue) formed from methacrolein and other isoprene products are added, and the total acyl peroxy radical model species (RCO3·) is removed. The need for RCO3· is eliminated by treating all the acyl peroxy radical model species as active, and including all their cross reactions. Although this requires more reactions and active species in the mechanism than the approach used previously, it gives a somewhat more accurate representation of the peroxy + peroxy reactions of these species, which can be important at nighttime, and eliminates the need to include a separate total peroxy radical operator as a co-product in every reaction forming such radicals.

T-Butoxy Radicals. As indicated above, most alkoxy radicals are not represented explicitly in the mechanism, but are replaced by the set of species they are assumed to form when they react. In the previous mechanism this was the case for all organic alkoxy radicals except for phenoxy (see below), and in particular, t-butoxy radicals were assumed to react exclusively by decomposition to acetone and methyl radicals. However, the decomposition of t-butoxy is believed to be relatively slow (see Table 46), and if NO<sub>2</sub> levels are sufficiently high then reaction with NO<sub>2</sub> may be non-negligible in high-NO<sub>x</sub> scenarios or

chamber experiments. In particular, the reaction of t-butoxy with  $\text{NO}_2$  had to be included for the model to appropriately simulate results of incremental reactivity chamber experiments with isobutane (Carter et al, 1993a). Because the competition between decomposition and  $\text{NO}_2$  depends on the  $\text{NO}_2$  concentration, this requires that t-butoxy radicals be represented explicitly in the model. This is not necessary for most other alkoxy radicals, which can either react sufficiently rapidly with  $\text{O}_2$ , or have sufficiently rapid decomposition or isomerization pathways, that reaction with  $\text{NO}_2$  can be neglected.

Phenoxy Radicals. Phenoxy radicals are represented explicitly in this and the previous mechanism because they are not expected to react with  $\text{O}_2$  and have no known rapid decomposition pathway. In the presence of  $\text{NO}_x$ , the major fate of phenoxy radicals is believed to be reaction with  $\text{NO}_2$ , since it has no obvious unimolecular reaction route or mechanism for reaction with  $\text{O}_2$ . (Reaction with  $\text{NO}$  would be expected to form a nitrite that would rapidly photolyze to re-form  $\text{NO}$  and phenoxy.) Nitrophenol formation has generally been assumed in this reaction (e.g., see Atkinson, 1990; Carter, 1990), presumably via some rearrangement of an initially formed unstable adduct. However, based on lower than expected yields of Nitrophenol in  $\text{NO}_3$  + cresol and  $\text{OH}$  + benzaldehyde systems (Atkinson, 1994), this may be an oversimplification. In the absence of  $\text{NO}_x$ , the major fate of phenoxy is assumed to be reaction with  $\text{HO}_2$ , though the model also includes a slow unimolecular loss to account for situations where  $\text{NO}_2$  or  $\text{HO}_2$  may be low. Note that the phenoxy radical model species is used as a surrogate for substituted phenoxy radicals as well, except for lumped nitro-substituted phenoxy radicals, discussed below.

Nitro-Phenoxy Radicals. Although their reaction mechanisms are assumed to be the same as phenoxy radicals, the  $\text{NO}_2$ -substituted phenoxy radicals assumed to be formed from the reactions of  $\text{NO}_3$  with phenols are represented separately. This is done to account for nitrogen balance, and because the dinitroaromatics expected to be formed in the reaction with  $\text{NO}_2$  are expected to be either non-volatile or non-reactive, and are thus represented in the model as “lost nitrogen”. This is the same representation as used in the previous mechanisms.

Formaldehyde +  $\text{HO}_2$  Intermediate. The radical believed to be formed when  $\text{HO}_2$  reacts with formaldehyde has to be represented explicitly because its subsequent fate is believed to be affected by  $\text{NO}$  levels, as shown on Table 46. The mechanism used is based on the IUPAC (Atkinson et al, 1999) recommendation, and is essentially the same as used in the previous mechanism.

#### **d. Peroxy Radical Operators**

Representation of peroxy radical reactions in mechanisms is complicated by the fact that a relatively large number of such radicals are formed even in condensed mechanisms, and they can react to a non-negligible extent with themselves and other peroxy radicals under some conditions. The approach employed in the Carter (1990) mechanism is to represent organic peroxy radicals with the set of products they would ultimately form if they reacted fully in the presence of  $\text{NO}_x$  and sunlight, together with a set of chemical “operators” that represent their other effects on the system. A total peroxy radical operator ( $\text{RO}_2\cdot$ ) is used to compute the total peroxy radical concentrations for the purpose of computing peroxy + peroxy radical reaction rates; this allows the steady-state approximation to be used for the other peroxy radical operators.

The approach used in this mechanism is similar, except that as indicated above it is not used for methyl peroxy because it is now represented explicitly, and also the total peroxy radical species ( $\text{RO}_2\cdot$ ) is eliminated. Instead of the latter, all the peroxy radical operators are treated as active species, and the cross-reactions between the operators are included. The elimination of  $\text{RO}_2\cdot$  simplifies the representation of peroxy radical chemistry and reduces the total number of species in the mechanism,

though at the expense of having a somewhat larger number of active species and peroxy + peroxy radical cross reactions. The number of peroxy radical operators used to represent organic nitrate formation was reduced to reduce the number of species and cross-reactions. The peroxy radical operators employed in this mechanism are summarized below.

**RO2-R.** This operator represents the effect of peroxy radical reactions that ultimately cause one NO to NO<sub>2</sub> conversion and formation of HO<sub>2</sub> when they react with NO. It is representing as having zero carbons. When this operator reacts with HO<sub>2</sub>, it is represented as forming ROOH, the lumped higher hydroperoxide species. Unlike the previous mechanism (Carter, 1990), which used a zero-carbon lumped hydroperoxide operator (-OOH) to represent the effect of hydroperoxide photolysis to form radicals, in this mechanism the higher hydroperoxides are represented by a model species whose reactions are based on those estimated for n-propyl hydroperoxide. In other words, a lumped molecule approach is used rather than the lumped structure approach. Since the organic portion of the radicals already represented by the products formed if the radical reacted with NO (which is why the RO2-R· operators are zero carbon species), formation of the ROOH in the HO<sub>2</sub> reaction does not conserve carbon. To account for this, loss of three “lost carbon” (XC) species are included in this reaction to main carbon balance. Although this may appear to be a worse approximation than using a zero-carbon lumped structure species such as the -OOH in the previous mechanism, in fact for most radicals carbon is lost in the model when the peroxy reacts with NO (because of the use of relatively small products to represent most of the lumped products), so this tends to work towards compensating for that effect. Tracing the “lost carbon” (XC) levels in the model can be used to track the extent to which carbon is lost due to the way the product species are represented.

When this operator reacts with explicitly the represented radical species [i.e., NO<sub>3</sub>, methyl peroxy, or any of the acyl peroxy species] the products formed are the same as would be formed if ethyl peroxy (CH<sub>3</sub>CH<sub>2</sub>OO·) reacted with those species, except that any C<sub>2</sub> organic products (acetaldehyde or ethanol) are removed, and if ethoxy radicals are formed, they are replaced by HO<sub>2</sub> (based on the fact that ethoxy can be represented as rapidly forming acetaldehyde + HO<sub>2</sub>, with acetaldehyde removed). In other words, since the RO2-R· does not represent the organic portions of the peroxy radicals, the organic products formed in its reactions are ignored. Note that it is assumed that in RO<sub>2</sub>· + RO<sub>2</sub>· reactions it is assumed that formation of 2 RO· + O<sub>2</sub> and disproportionation to an alcohol + a carbonyl + O<sub>2</sub> occur with equal probability, based on available data for higher peroxy radicals (Atkinson et al, 1999). In the case of reaction of methyl peroxy, it is assumed that the disproportionation forming methanol and that forming formaldehyde occur with equal probability.

**R2O2.** This represents the effects of extra NO to NO<sub>2</sub> conversions caused by multi-step reaction mechanisms, as would occur, for example, in mechanisms involving alkoxy radical decompositions or isomerizations. Again, R2O2· is used so the model can account for the formation of RO<sub>2</sub>, and [R2O2] is used for the actual reactions of the operator. Unlike the RO2-R· and the other peroxy operators, this is not strictly speaking a radical species, and it is not represented as having any effect on the system except when it reacts with NO. This is because it does not react to form radical or radical sink species, and is only appropriately used in conjunction with RO2-R.

**RO2-N.** This represents the reactions of peroxy radicals with NO forming organic nitrates of various types, which are all represented in the model by the 6-carbon lumped alkyl nitrate model species RNO<sub>3</sub> (see Section 3.b). Note that in previous versions of the mechanisms two additional operators were used to represent these processes: RO2-XN· was used to represent peroxy radicals that reacted with NO to form relatively unreactive C<sub>3</sub> nitrates, and RO2-XN· was used to represent aromatic peroxy radicals that reacted with NO to form aromatic nitrates. In this mechanism RO2-XN· was removed because the amount

of C<sub>3</sub> nitrate formation tends to be extremely small, and RO<sub>2</sub>-NP· was removed nitrate formation is assumed to be relatively minor for most aromatics. In addition, the reactions of the aromatic nitrates formed are so uncertain that representing them separately may not necessarily be any more accurate than lumping them with RNO<sub>3</sub>.

Since the RO<sub>2</sub>-N· operator is used to represent the organic nitrates formed when the peroxy radicals react with NO, it is represented as having the number of carbons of the nitrate it forms when it reacts with NO, and its reactions with species other than NO are based on this representation. The products are derived based on what is considered to be appropriate for a C<sub>6+</sub> alkyl peroxy radical, since those tend to be the radicals that are the largest precursors to alkyl nitrates in atmospheric simulations. In addition, since primary radicals tend to be formed in lower relative yields from such higher molecular weight compounds than secondary or tertiary radicals (because the C-H bonds tend to be more labile), the carbonyl products are represented by ketone model species (MEK or PROD2), rather than by aldehydes. The specific products used are indicated in the footnotes to Table 46 for the various reactions.

RO<sub>2</sub> + RO<sub>2</sub> Reactions. Because the rate constants for peroxy + peroxy radical reactions can vary by orders of magnitude depending on the type of radical (e.g., Atkinson, 1997), the rate constant used for the peroxy + peroxy reactions of the peroxy radical operators must necessarily be very approximate. The value used for all these operators is based roughly on the range of rate constants for secondary peroxy radicals given by Atkinson (1997a) and Atkinson et al (1997b), and is 30 times higher than the 1 x 10<sup>-15</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> value used in the previous mechanism (Carter 1990).

### 3. Reactions of Common Products

A total of 24 model species are used in this mechanism to represent the reactive organic product species, 11 of which are used for organic compounds that are represented explicitly, and 13 of which are used to represent groups of similar products using the “lumped molecule” approach. In most cases, the model species and mechanisms are not significantly different than in previous versions of the mechanisms, except that some of the rate constants were updated as indicated in footnotes to Table 46. Most of the updates for the C<sub>3</sub> products are based on IUPAC (Atkinson et al, 1997a, 1999) recommendations. The species used are summarized below.

#### a. Explicitly Represented and Lumped Molecule Products

Formaldehyde (HCHO) and Acetaldehyde (CCHO). The mechanisms for these two compounds are essentially the same as in the previous mechanism, except that some of the rate constants and absorption cross sections have been updated as recommended by IUPAC (Atkinson et al, 1997a, 1999). Note that this mechanism differs from most condensed mechanisms in that acetaldehyde is represented explicitly, with most higher aldehydes lumped with propionaldehyde, as discussed below. The one exception is glycolaldehyde (HOCH<sub>2</sub>CHO), which is expected to have a reactivity closer to acetaldehyde than propionaldehyde, and therefore is represented by acetaldehyde in this mechanism.

Propionaldehyde and Lumped Higher Aldehydes (RCHO). The reactions of the model species RCHO, which represents all C<sub>3+</sub> aldehydes except glycolaldehyde, α-dicarbonyls, aromatic aldehydes, and acroleins, is based on the expected mechanism for propionaldehyde. Note that, based on structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), approximately 4% of the reaction with OH radicals is estimated to occur by abstraction from the CH<sub>2</sub> group and ~1% at the methyl. The reactions of the radicals subsequently formed are derived using the general mechanism estimation methods, as discussed below. However, most of the OH reaction is analogous to the reaction of OH with acetaldehyde, forming RCO-O<sub>2</sub>·, the lumped higher acyl peroxy

radical. The  $\text{NO}_3$  and photolysis reactions are also assumed to be analogous to those for acetaldehyde, though a slightly higher  $\text{NO}_3$  radical rate constant is assumed (based on the somewhat higher OH rate constant), and absorption cross sections and quantum yields specific to propionaldehyde are used.f

Acetone (ACET). Acetone is represented explicitly because it has significantly lower reactivity than other ketones, yet is sufficiently reactive that its reactivity is probably not negligible in long-range transport scenarios. Its mechanism is based on that discussed by Carter et al (1993b). Based on the data of Jenkin et al (1993), the  $\text{CH}_3\text{COCH}_2\text{O}\cdot$  radical is believed to primarily decompose to formaldehyde and  $\text{CH}_3\text{CO}\cdot$ . The absorption cross sections and quantum yields are based on the IUPAC (Atkinson et al, 1997a), except that the reported quantum yields at 230 and 330 nm are believed to be high, and were corrected as discussed by Carter et al (1993b) and the footnotes to Reaction K3HV on Table 46. Note that the data of Carter et al (1993b) indicate that these quantum yields, even after adjustment, tend to slightly overpredict the reactivity of acetone in indoor and outdoor chamber experiments (see Section ?? for a discussion of the results of the evaluation of the mechanism against chamber data).

Methyl Ethyl Ketone and Lumped Lower Reactivity Ketones (MEK). This model species is used to represent ketones and other reactive oxygenated product species whose OH radical rate constant is between  $5 \times 10^{-13}$  and  $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . Note that this is different from previous versions of the SAPRC mechanism, where MEK was used for all higher non-aldehyde, non-aromatic oxygenated products that were more reactive than acetone. The MEK mechanism is based on that derived for methyl ethyl ketone using the general mechanism estimation methods discussed below, the IUPAC recommended OH rate constant (Atkinson et al, 1999) and absorption cross sections provided by Moortgat (private communication, 1996). The overall photolysis quantum yield of 15% was derived by fits to MEK -  $\text{NO}_x$  and MEK incremental reactivity environmental chamber experiments carried out in our laboratories (see Section ?? and Carter et al, 1999a), and is somewhat higher than the ~10% overall quantum yield derived previously based on fits to a few UNC outdoor chamber experiments (Carter, 1990; Carter and Lurmann, 1991).

Methanol (MEOH). In previous SAPRC mechanisms methanol in emissions was represented as an assigned parameter detailed model species, which permitted it to be represented explicitly or lumped with other compounds, depending on the model application. However, this approach does not permit representing formation of methanol as a reaction product. In this mechanism methanol is assigned an explicit model species in order to permit its formation of a product in no- $\text{NO}_x$  reactions of methyl peroxy reaction. These reactions, and the subsequent reactions of methanol so formed, may be non-negligible in some long-range transport scenarios. Since methanol is potentially important in emissions, most model applications would probably use a separate model species for it in any case. Indeed, methanol is now represented explicitly even in some condensed models such as expanded Carbon Bond IV (e.g., Carter, 1994b and references therein). The mechanism is based on IUPAC (Atkinson et al, 1997a, 1999) recommendations.

Methyl Hydroperoxide (COOH) and Lumped Higher Peroxides (ROOH). In previous SAPRC mechanisms, the hydroperoxide species formed in peroxy +  $\text{HO}_2$  reactions were represented by a single “lumped structure” model species “-OOH”, combined with the organic products formed in the peroxy + NO reactions. In this mechanism, for more accurate representation of low- $\text{NO}_x$  chemistry, for regional or long-range transport simulations, methyl hydroperoxide is represented explicitly, and the other hydroperoxides are represented using a separate model species (ROOH) using the “lumped molecule” approach. In the case of methyl hydroperoxide, the OH reaction is assumed to occur at both the methyl and OOH positions as recommended by IUPAC (Atkinson et al, 1997a, 1999), with the  $\cdot\text{CH}_2\text{OOH}$  radical



formed in the former reaction being assumed to rapidly decompose to formaldehyde + OH. The absorption cross sections are also based on IUPAC recommendations, with unit quantum yields assumed, and with the reaction assuming to proceed entirely by breaking the weak O-O bond.

The reactions of the lumped higher hydroperoxide (ROOH) are based on the estimated mechanism for n-propyl hydroperoxide. As discussed in footnotes to Table 46 in Table 47, the OH reaction is estimated to occur at the OOH group ~2/3 of the time, based on assuming the same rate constant as the same reaction of methyl hydroperoxide. Most of the remainder of the reaction is assumed to occur at the 1-position, yielding an  $\alpha$ -hydroperoxy radical which is assumed to rapidly decompose to propionaldehyde (RCHO) and OH. The photolysis is assumed to have the same rate and an analogous mechanism as methyl hydroperoxide.

Glyoxal (GLY). Glyoxal, which is formed in the reactions of most aromatics, acetylene, and some other species [including some isoprene oxidation products (Carter and Atkinson, 1996)], continues to be represented explicitly in this mechanism. Since it is less reactive than some other aromatic products it is often not represented in condensed mechanisms, but it is known to make an important contribution to the reactivity of acetylene (Carter et al, 1997c) and benzene (see Section ??) and its reactivity is not well approximated by other model species. On the hand, this mechanism is somewhat more condensed than previous detailed SAPRC mechanisms in that the acyl peroxy radical and PAN analogue predicted to be formed from the OH + glyoxal reaction [ $\text{HCO}(\text{CO})\text{OO}\cdot$  and  $\text{HCO}(\text{CO})\text{OONO}_2$ ] are not represented explicitly, but are lumped with RCO-O $\cdot$  and PAN2 (see below). The mechanism for the OH reaction is based on the data of Niki et al (1985) as discussed by IUPAC (Atkinson et al, 1997a).

The glyoxal absorption cross sections were the same as used previously (Plum et al, 1983), as recommended by the IUPAC evaluation (Atkinson et al, 1997a). However, the quantum yields were significantly revised based modeling of acetylene - NO $_x$  and acetylene reactivity environmental chamber data (Carter et al, 1997c), as discussed in the footnotes to Table 46 in Table 47. The model simulations of those chamber experiments were found to be highly sensitive to glyoxal absorption cross sections used in the mechanism, and no other reasonable adjustments to the mechanism would yield acceptable fits to the data (Carter et al, 1997c). Note that to fit the data quantum yields which are ~1.4 times higher than overall quantum yield reported by Plum et al (1983) for conditions of those experiments must be used. Although use of acetylene reactivity data is a highly indirect way to obtain glyoxal quantum yields, we consider it to be a less uncertain way to estimate radical quantum yields than the data of Plum et al (1993), which uses a UV-poor light source, only measures rates of glyoxal decay. Clearly this is uncertain and direct measurements of glyoxal quantum yields as a function of wavelength are needed.

Methyl Glyoxal (MGLY) and Other Higher  $\alpha$ -dicarbonyl aldehydes. Methyl glyoxal is formed in the reactions of methylbenzenes and from some carbonyl compounds is a highly reactive compound that can significantly affect the reactivity of compounds that form it. The MGLY model species is also used to represent other  $\alpha$ -dicarbonyl aldehydes, such as ethylglyoxal, etc. However, unlike the SAPRC-97 mechanism of Carter et al (1997a), but like earlier versions of the mechanism (Carter, 1990, 1995; Carter et al, 1993b), it is not used in this version of the mechanism to represent any of the uncharacterized aromatic ring fragmentation products (see discussion of unknown aromatic fragmentation products, below). The mechanism for the OH and NO $_3$  reactions are similar to those in the previous mechanism, with the latter reaction assumed to have the same rate constant and analogous mechanism as for acetaldehyde.

The IUPAC recommended (Atkinson et al, 1997a, 1999) absorption cross sections for methyl glyoxal are approximately a factor of 2 higher than the Plum et al (1983) values used in the previous mechanism. The current mechanism uses cross sections obtained from Moortgat (personal communication, 1996), which are consistent with the IUPAC recommendations but have higher resolution. Unit quantum yields were assumed in the low wavelength band ( $\lambda \leq 340$  nm) and zero quantum yields were assumed for wavelengths above the cutoff of 421 nm, as determined by the thermochemistry. For the rest of the high wavelength regime, the quantum yield was assumed to decline linearly from unity at 344 nm to zero at a wavelength (407 nm) that was adjusted such that the calculated overall photolysis rates under the conditions of the experiments of Plum et al (1983) agreed with the experimentally measured values. (An analogous treatment was used in when deriving the quantum yields for glyoxal and biacetyl, though in the glyoxal case the adjustment was to fit the acetylene chamber data, as indicated above.) Note that this gives a different wavelength dependence than assumed in the previous mechanism, where a wavelength-dependent overall quantum yield was assumed for the entire high-wavelength band, including wavelengths above the high wavelength cutoff.

Biacetyl (BACL) and Other  $\alpha$ -Dicarbonyl Ketones. Biacetyl or other  $\alpha$ -dicarbonyl ketones are formed in significant yields from p-xylene, 1,2,4-trimethylbenzene and other o-dimethyl aromatics, and might be formed from the reactions of some carbonyl compounds. Biacetyl was not represented in previous versions of the mechanism, being in effect represented by methyl glyoxal. However, because its chemistry is in some ways quite different from methyl glyoxal (it reacts only slowly with OH, and its photolysis forms only PAN precursors), it was decided to represent it explicitly in this mechanism. The BACL model species is also used for other  $\alpha$ -dicarbonyl ketones.

The reaction of biacetyl with OH radicals is ignored because the OH + biacetyl rate constant is probably not much different than that for acetone, making it a negligible loss process compared to photolysis. The photolysis is assumed to proceed via breaking the weak CO-CO bond, as shown on Table 46. The absorption cross sections used were those from Plum et al (1983), and the wavelength-dependence of the quantum yields were derived from the data of Plum et al (1983) in a manner exactly analogous to that discussed above for methyl glyoxal (see footnotes to Table 46 in Table 47).

Phenol (PHEN) and Cresols (CRES). Phenol is formed from the reactions of benzene and is represented as being formed in the subsequent reactions of aromatic ring-retaining products such as cresols or benzaldehydes, and cresols are formed in the reactions of the substituted aromatics. Cresol is used to represent phenolic products formed from all alkyl-substituted benzenes, while phenol is used to represent such products formed from benzene and naphthalene, as well as phenolic products formed in secondary reactions of cresols. The relatively rapid reactions of these compounds with NO<sub>3</sub> represents a NO<sub>x</sub> sink in the aromatic mechanisms that largely explains their predicted tendency to inhibit O<sub>3</sub> under low NO<sub>x</sub> conditions. Therefore, it is important that these model species be in the mechanism. . They are kept as separate model species because the reactions of cresols are assumed to involve some PAN (or PAN analogue) formation, while this is assumed not to be the case for phenol.

There are still inadequate data concerning the atmospheric reactions of these compounds and the products they form, and the highly parameterized mechanisms used in the previous versions of the SAPRC mechanisms are essentially unchanged in this version. The main consumption reactions are with OH and NO<sub>3</sub>, and the rate constants used are those recommended by Atkinson (1994). The OH + cresol mechanism is based on the highly parameterized mechanism derived by Carter (1990), but the version for this mechanism was reoptimized to fit the data from the single o-cresol - NO<sub>x</sub> chamber experiment EC281 (Pitts et al, 1979; Carter et al, 1995d). The OH + phenol mechanism was derived by analogy with the

resulting cresol mechanism. The  $\text{NO}_3$  reactions are assumed to proceed via the formation of phenoxy radicals +  $\text{HNO}_3$  (with the BZ-O $\cdot$ ) model species used for substituted as well as unsubstituted radicals, when then reacts as discussed above in Section 2.c. Note that although the mechanism for the  $\text{NO}_3$  reaction (like that for the reaction with OH) is highly uncertain, it clearly must involve some sort of  $\text{NO}_x$  sink process in order for model simulations to fit chamber data for aromatics.

Nitrophenols (NPHE). The “nitrophenol” model species is used to represent whatever products are formed when phenoxy reacts with  $\text{NO}_2$ , which as indicated above is uncertain. It is assumed that the  $\text{NO}_2$ -substitution slows down the rate of reaction with OH radicals, and that its only significant consumption process is reaction with  $\text{NO}_3$ , for which it is assumed to have the same rate constant as phenol. This representation is unchanged from previous versions of the mechanism. Obviously this aspect of the mechanism is uncertain, but this representation appears to perform reasonably well in simulating effects of aromatics on peak  $\text{O}_3$  yields, which are determined by  $\text{NO}_x$ -sink processes that are represented by the formation and reactions of NPHE.

Benzaldehyde (BALD) and Other Aromatic Aldehydes. Benzaldehyde, tolualdehydes and other aromatic aldehydes that are formed in a minor but non-negligible route in the reactions of OH with methylbenzenes are represented by the benzaldehyde (BALD) model species. Its OH and  $\text{NO}_3$  reactions are assumed to be analogous to other aldehydes, except that separate model species (BZCO-O2 $\cdot$  and BZ-PAN) are used to represent the acyl peroxy radical and PAN analogue formed. This is necessary because the reaction of the benzoyl peroxy radical with NO forms phenoxy radicals, which does not regenerate radicals like the radicals formed when the other acyl peroxy radicals react with NO.

The absorption cross sections for benzaldehyde (Majer et al, 1969) indicate that its photolysis can be significant if the quantum yield is sufficiently high. The quantum yields are unknown, but chamber data indicates that it is probably consumed to a non-negligible by photolysis, though the overall quantum yield is relatively low and the photolysis apparently does not involve significant radical formation. The overall quantum yield derived by Carter (1990) to fit SAPRC evacuable chamber data (Pitts et al, 1979) is retained in this mechanism. It was found to give reasonably good model simulations of benzaldehyde -  $\text{NO}_x$  experiments carried out in the CE-CERT Xenon Teflon Chamber (Carter et al, 1998a).

Methacrolein (METHACRO) and Methyl Vinyl Ketone (MVK). This version of the mechanism incorporates the “four product” isoprene mechanism (Carter, 1996) as part of the base mechanism, so it includes model species for methacrolein, MVK, and the lumped other isoprene products (ISOPROD). The mechanisms used for methacrolein and MVK are essentially the same as derived by Carter and Atkinson (1996), with some minor updates as indicated in footnotes to Table 46 in Table 47. The mechanisms were generated using the mechanism generation system discussed in Section ??, which incorporated most of the estimates and assignments of Carter and Atkinson (1996) for the reactions specific to the isoprene and isoprene product system. This resulted in some minor changes to yields of minor product in some reactions. In addition, because of these changes and changes to the overall base mechanism, the overall quantum yield for the methacrolein MVK photolysis was reoptimized, using the same procedures and data as discussed by Carter and Atkinson (1996). This resulted the overall quantum yield for methacrolein being increased by ~14%, while that for MVK was reduced by over a factor of ~5. The reason for this large change in the optimized MVK quantum yield is not clear, but it may be due to a relatively low sensitivity of model simulation results to large changes in this parameter. (See Section ?? for results of model simulations of the methacrolein and MVK experiments.)

Methacrolein is also used to represent acrolein in reactions where acrolein is predicted to be formed as a product. This is to avoid adding a new model species to represent a relatively minor

product in most ambient mixtures. However, as discussed in Section ??, this mechanism has a separate detailed model species for acrolein with mechanistic assignments appropriate for this compound, which can be used to more accurately represent acrolein when its reactivity is being assessed, or when emitted directly.

Lumped Isoprene Products (ISOPROD). The ISOPROD model species is used to represent reactive isoprene products other than methacrolein and MVK, and also to represent other unsaturated ketones or aldehydes (other than acrolein itself, which is represented by methacrolein) when formed in reactions of other VOCs. Its mechanism is based on the ISOPROD model species in the “four product” isoprene mechanism of Carter (1996), with some minor modifications as indicated in footnotes to Table 46 in Table 47. Its mechanism is derived from weighted averages of rate constants and parameters for a mixture of 30% hydroxymethacrolein and 23⅓% each *cis*-HCOC(CH<sub>3</sub>)-CHCH<sub>2</sub>OH, *trans*-HCOC(CH<sub>3</sub>)-CHCH<sub>2</sub>OH, and HCOCH=C(CH<sub>3</sub>)CH<sub>2</sub>OH. As with methacrolein and MVK, the mechanisms for these species were derived using the mechanism generation system discussed in Section ??, incorporating estimates and assignments of Carter and Atkinson (1996) where applicable. The mechanisms derived for these individual species are given with those for the other detailed model in Section ??.

#### **b. Lumped Parameter Products**

“Lumped parameter” species refer to model species whose mechanisms are derived by averaging rate constants and product yield parameters from a representative mixture of compounds that they are designed to represent. Although the previous versions of the SAPRC mechanism used this approach only for model species representing emitted VOCs, this mechanism also uses this approach for two of the lumped organic product species, as discussed below.

Lumped Higher Reactivity Non-Aldehyde Oxygenates (PROD2). This model species, which is new to this version of the mechanism, is used to represent ketones, alcohols, and other reactive non-aromatic and non-double-bond-containing oxygenated products whose rate constants are higher than  $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . This was added because it was judged that many of the bi- or polyfunctional product species that were previously represented by MEK when they were formed as products are in fact much more reactive than MEK, at least in terms of their reaction rate with OH radicals. The reaction mechanism of PROD2 is based on averaging mechanisms derived for a representative set of product species as discussed below.

Lumped Organic Nitrate Products (RNO3). This model species is used to represent various organic nitrates (other than PAN or PAN analogues), primarily those formed in the reactions of peroxy radicals from NO. This is consumed primarily by reaction with OH radicals, but a slow photolysis, which may be non-negligible in long-range transport simulations, is also included in the mechanism. Unlike previous SAPRC mechanisms, RNO3 is also used to represent those formed from aromatic peroxy radicals with NO; previously the nitrophenol (NPHE) model species was used for this purpose. As indicated above, this change was made to avoid having to add the separate peroxy radical “operator” needed to support separate representation of aromatic nitrates, which are formed in relatively low yields and for which the appropriateness of the NPHE vs the RNO3 representation is unknown. The reaction mechanism of RNO3 is based on averaging mechanisms derived for a representative set of product species as discussed below.

Derivation of PROD2 and RNO3 Mechanisms. Although in principle the mechanisms for the lumped parameter product species can be derived for each emissions inventory in the manner used for the lumped parameter model species used for emitted VOCs (see Section ??), the necessary software to do

this has not yet been developed. Instead, in this version of the mechanism the parameters are derived from sets of representative species representing products predicted to be formed from the reactions of the mixture of VOCs used as the “Base ROG” mixture in the atmospheric reactivity calculations (Carter, 1994a; see also Section ??), and are held fixed in the model simulations. The Base ROG mixture is used to represent reactive VOCs from all sources, and is derived from the “all city average” mixture derived by Jeffries et al (1989) from analysis of air quality data, with minor modifications as discussed by Carter (1994a,b)<sup>1</sup>. For the purpose of determining the contributions of the reactions of the compounds in the mixture to the formation of a lumped product, the contribution of each emitted VOC is weighed by the amount of each VOC that is estimated to react in a one-day scenario, multiplied by the yield of the lumped product used in the model for the reactions of the VOC. The amount reacted is obtained from the amount emitted multiplied by the “mechanistic reactivity” (Carter and Atkinson, 1989; Carter, 1994a), which is the fraction of the VOC estimated to react. The latter is obtained from mechanistic reactivities in the “averaged conditions” scenario where the NO<sub>x</sub> inputs are adjusted to yield maximum peak ozone concentrations (the “MOIR” scenario)<sup>2</sup> (Carter, 1994; see tabulation in Section ?? for the values used). Table 1 and Table 2 show the contributions of the reactions of various types of VOCs in the base ROG mixture to the formation of the RNO3 and PROD2 model species.

The set of compound that are represented by various model species can be calculated for those model species whose mechanisms can be derived using the mechanism generation/estimation system that is discussed in Section II.B. For each of these compounds, the system generates the set of products that are predicted to be formed using a fully explicit mechanism for the reactions in the presence of NO<sub>x</sub>, which are then used, together with the “lumping rules” discussed in Section II.B.12, to determine the lumped product yields for the model. From this, the distribution of individual product VOCs represented by each lumped product model species can be determined, at least for the reactions of the VOCs whose mechanisms can be generated using this system. Although this system cannot generate mechanisms for aromatic compounds and terpenes, for which parameterized mechanisms must still be used, Table 1 and Table 2 show that their contributions to PROD2 or RNO3 formation from the base ROG mixture is minor. In particular, reactions of aromatics and terpenes account for less than 6% of the PROD2 formation, and for less than 5% of the formation of RNO3 in one-day scenarios.

Table 3 and Table 4 show the 35 most important products predicted to be formed from the reactions of the VOCs in the base ROG mixture that are represented by PROD2 (Table 3) or RNO3 (Table 4). The tables also show the contribution of each product to the total of all products represented by PROD2 or RNO3, their OH radical rate constant and carbon numbers, and the average OH rate constant and carbon number for all the products, weighed by their molar contribution to the total. Note that no single compounds dominate the lists, and in the case of the organic nitrates the top 35 compounds account for less than half of the products formed that are represented by RNO3. Therefore, in both cases there is no obvious choice of a single “representative” or “typical” compound to use for lumped molecule representations.

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<sup>1</sup> The complete mixture, indicating the specific detailed model species used to represent it in the model, is given in Section ???. See also Carter (1994b).

<sup>2</sup> The MOIR mechanistic reactivities are used because they are typical mechanistic reactivities in a wide range of scenarios. MIR mechanistic reactivities tend to be lower than in other scenarios because the relatively high NO<sub>x</sub> levels tend to suppress radical levels.

Table 1. Contributions of various types of model species in the base ROG mixture to the formation of the PROD2 lumped product species.

VOC	Cont'n	VOC	Cont'n	VOC	Cont'n	VOC	Cont'n
N-C5	14.5%	4-ME-C7	2.9%	1-C9E	1.0%	3-ME-C11	0.3%
N-C10	8.1%	1-HEPTEN	2.7%	24-DM-C5	0.9%	26DM-C9	0.2%
N-C6	6.2%	24-DM-C7	2.5%	3-ME-C6	0.9%	ME-CYCC6	0.2%
N-C7	5.8%	3-ME-C6	2.2%	1-HEXENE	0.8%	1-C10E	0.2%
<u>Aromatics</u>	<u>5.2%</u>	2-ME-C6	1.9%	N-C11	0.7%	4-ME-C10	0.2%
1-HEXENE	5.0%	4-ME-C8	1.9%	3-ME-C5	0.6%	3-ME-C10	0.2%
24-DM-C6	4.5%	2-ME-C8	1.8%	36DM-C10	0.6%	1-PENTEN	0.1%
2-ME-C7	4.2%	26DM-C8	1.7%	24-DM-C5	0.5%	23-DM-C5	0.1%
2-ME-C5	3.6%	4-ME-C9	1.6%	1-OCTENE	0.5%	1-PENTEN	0.1%
N-C8	3.5%	2-ME-C9	1.6%	ET-CYCC6	0.4%	N-C13	0.1%
N-C9	3.4%	N-C12	1.4%	1-C11E	0.3%	2-ME-C5	0.1%
CYCC6	3.0%	ME-CYCC6	1.1%	5-ME-C11	0.3%	3M-1-BUT	0.0%

Table 2. Contributions of various types of model species in the base ROG mixture to the formation of the RNO3 lumped product species.

VOC	Cont'n	VOC	Cont'n	VOC	Cont'n	VOC	Cont'n
2-ME-C4	7.7%	23-DM-C5	1.6%	N-C11	0.6%	C-2-BUTE	0.2%
N-C4	5.9%	<u>Terpenes</u>	<u>1.4%</u>	1-C11E	0.5%	1-PENTEN	0.2%
N-C10	5.8%	24-DM-C5	1.3%	ET-CYCC6	0.5%	1-C10E	0.2%
24-DM-C6	4.9%	2-ME-C3	1.3%	2M-1-BUT	0.5%	1-BUTENE	0.2%
N-C5	4.9%	2-ME-C9	1.3%	1-OCTENE	0.5%	1C6RCHO	0.2%
2-ME-C5	4.0%	2-ME-C8	1.3%	T-3-C7E	0.5%	T-2-C7E	0.2%
ME-CYCC5	3.1%	4-ME-C9	1.2%	1-PENTEN	0.4%	13-BUTDE	0.2%
<u>Aromatics</u>	<u>2.7%</u>	4-ME-C8	1.2%	PROPENE	0.4%	3M-1-BUT	0.2%
24-DM-C7	2.5%	1-C9E	1.2%	T-4-C9E	0.4%	T-4-C10E	0.2%
26DM-C8	2.5%	PROPANE	1.2%	T-2-C6E	0.4%	3-ME-C10	0.1%
3-ME-C5	2.4%	N-C12	1.1%	C-2-C6E	0.4%	1C5RCHO	0.1%
2-ME-C7	2.4%	CYCC5	1.0%	T-5-C11E	0.4%	4-ME-C10	0.1%
N-C7	2.4%	2-ME-C6	0.9%	22-DM-C4	0.3%	CYC-HEXE	0.1%
4-ME-C7	2.3%	CYCC6	0.9%	T-2-BUTE	0.3%	MEK	0.1%
3-ME-C6	2.1%	ISOBUTEN	0.9%	ME-CYCC6	0.3%	23-DM-C4	0.1%
N-C9	2.1%	3-ME-C6	0.9%	3-ME-C11	0.3%	2-ME-C5	0.1%
N-C8	1.9%	23-DM-C4	0.9%	5-ME-C11	0.3%	3-ME-C5	0.1%
N-C6	1.8%	C-2-PENT	0.8%	26DM-C9	0.3%	N-C13	0.1%
1-HEPTEN	1.8%	T-2-PENT	0.8%	T-4-C8E	0.3%	36DM-C11	0.0%
ME-CYCC6	1.7%	24-DM-C5	0.7%	2M-2-BUT	0.3%		
1-HEXENE	1.7%	36DM-C10	0.6%	1-HEXENE	0.2%		

Table 3. Product compounds predicted to be formed in the atmospheric reactions of compounds in the base ROG mixture that are represented by the PROD2 model species.

Cont'n [a]	kOH [b]	nC [c]	Model Species [d]	Product Structure [e]
	<u>1.5e-11</u>	<u>7.19</u>		<u>Average of all Products</u>
16.4%	9.6e-12	5	PROD2-1	<u>CH3-CO-CH2-CH2-CH2-OH</u>
6.1%	1.7e-11	6		CH3-CH(OH)-CH2-CH2-CO-CH2-OH
3.8%	1.5e-11	6	PROD2-2	<u>CH3-CO-CH2-CH(CH3)-CH2-OH</u>
3.4%	6.4e-12	6		*CH2-CH2-CH2-CH2-CH2-CO-*
3.1%	1.4e-11	6		CH3-CH(OH)-CH2-CH2-CO-CH3
2.9%	1.1e-11	6		CH3-CH2-CO-CH2-CH2-CH2-OH
2.9%	2.0e-11	7		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-OH
2.7%	5.5e-12	6		CH3-CO-CH2-C(CH3)(OH)-CH2-OH
2.7%	1.5e-11	7	PROD2-3	<u>CH3-CH(OH)-CH2-CH2-CO-CH2-CH3</u>
2.3%	2.7e-11	5		CH3-CH(OH)-CH2-CO-CH3
2.2%	1.7e-11	7		CH3-CH2-CH(OH)-CH2-CH2-CO-CH3
2.2%	2.3e-11	10		CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
2.1%	2.1e-11	10		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3
2.0%	7.1e-12	8		CH3-C(CH3)(OH)-CH2-CH2-CO-CH2-CH3
1.7%	2.1e-11	10		CH3-CH2-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
1.5%	1.9e-11	7		CH3-CH(OH)-CH(CH3)-CH2-CO-CH3
1.3%	2.2e-11	8		CH3-CH2-CH(OH)-CH(CH3)-CH2-CO-CH3
1.3%	1.8e-11	8	PROD2-4	<u>CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3</u>
1.3%	6.0e-12	7		CH3-C(CH3)(OH)-CH2-CH2-CO-CH3
1.3%	2.4e-11	10		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH2-CH3
1.3%	1.9e-11	8		CH3-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
1.2%	7.4e-12	8		CH3-C(CH3)(OH)-CH2-CH(CH3)-CO-CH3
1.2%	1.7e-11	8		CH3-CH(OH)-CH2-CH(CH3)-CO-CH2-CH3
1.2%	1.4e-11	7		CH3-CH2-CH2-CO-CH2-CH2-CH2-OH
1.1%	1.6e-11	7		CH3-CH(OH)-CH2-CH(CH3)-CO-CH3
1.1%	1.9e-11	8		CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
1.1%	2.0e-11	9	PROD2-5	<u>CH3-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-CH3</u>
1.1%	2.2e-11	9		CH3-CH2-CH(OH)-CH2-CH2-CO-CH2-CH2-CH3
1.0%	1.4e-11	6		CH3-CH(CH3)-CH2-CO-CH3
1.0%	2.3e-11	9		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH2-OH
1.0%	2.2e-11	10		CH3-CH(OH)-CH2-CH2-CO-CH2-CH2-CH2-CH2-CH3
0.8%	2.0e-11	9		CH3-CH2-CH2-CH2-CH(OH)-CH2-CH2-CO-CH3
0.8%	1.9e-11	8		CH3-CH(CH3)-CH(OH)-CH2-CH2-CO-CH3
0.8%	1.7e-11	7		*CH(CH3)-CH2-CH2-CH2-CO-CH2-*
0.8%	1.7e-11	8		CH3-CH(OH)-CH2-CH2-CO-CH(CH3)-CH3
21.6%				All Others

[a] Amount of formation of this compound relative to all products represented as PROD2, on a molar basis.

[b] OH radical rate constant estimated using structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), in units of  $\text{cm}^3 \text{molec}^{-1} \text{sec}^{-1}$ .

[c] Number of carbons.

[d] Detailed model species name used when computing mechanism for compound that was used for deriving PROD2 mechanism for the model.

[e] Product structure as used in the mechanism generation system. The "\*" symbol is used to indicate groups that are bonded in cyclic compounds. Underlined structures are those used to derive the PROD2 mechanism.

Table 4. Product compounds predicted to be formed in the atmospheric reactions of compounds in the base ROG mixture that are represented by the RNO3 model species.

Cont'n [a]	kOH [b]	nC [c]	Model Species [d]	Product Structure [e]
	<u>7.8e-12</u>	<u>6.58</u>		Average of all Products
6.5%	1.6e-12	4	RNO3-1	<u>CH3-CH(ONO2)-CH2-CH3</u>
3.6%	3.0e-12	5		CH3-CH(CH3)-CH(ONO2)-CH3
2.8%	4.2e-13	3		CH3-CH(ONO2)-CH3
2.6%	1.7e-12	5		CH3-C(CH3)(ONO2)-CH2-CH3
2.5%	3.0e-12	5		CH3-CH(ONO2)-CH2-CH2-CH3
1.4%	2.8e-12	5		CH3-CH2-CH(ONO2)-CH2-CH3
1.0%	4.7e-12	6	RNO3-3	<u>CH3-CH(ONO2)-CH(CH3)-CH2-CH3</u>
1.0%	1.2e-11	5	RNO3-2	<u>CH3-CH(OH)-CH2-CH2-CH2-ONO2</u>
1.0%	5.1e-13	4		CH3-C(CH3)(ONO2)-CH3
1.0%	3.1e-12	6		CH3-C(CH3)(ONO2)-CH2-CH2-CH3
0.9%	4.5e-12	4		CH3-C(CH3)(ONO2)-CH2-OH
0.9%	4.2e-12	6		CH3-CH(CH3)-CH(ONO2)-CH2-CH3
0.9%	9.9e-12	10	RNO3-6	<u>CH3-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH3</u>
0.9%	9.9e-12	10		CH3-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH3
0.9%	9.9e-12	10		CH3-CH2-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH2-CH3
0.9%	5.6e-12	8	RNO3-5	<u>CH3-CH(CH3)-CH2-C(CH3)(ONO2)-CH2-CH3</u>
0.8%	9.9e-12	7	RNO3-4	<u>CH3-CH2-CH2-CH2-CH2-CH(ONO2)-CH2-OH</u>
0.8%	2.8e-12	6		CH3-CH2-C(CH3)(ONO2)-CH2-CH3
0.8%	1.0e-11	5		CH3-CH(OH)-CH(ONO2)-CH2-CH3
0.8%	1.2e-11	5		CH3-CH(ONO2)-CH(OH)-CH2-CH3
0.8%	4.4e-12	6		CH3-CH(CH3)-CH2-CH(ONO2)-CH3
0.8%	7.2e-12	6		*CH(ONO2)-CH2-CH2-CH2-CH2-CH2-*
0.7%	1.0e-11	10		CH3-CH(ONO2)-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH3
0.7%	6.2e-12	8		CH3-C(CH3)(ONO2)-CH2-CH(CH3)-CH2-CH3
0.7%	4.2e-12	7		CH3-CH2-C(CH3)(ONO2)-CH2-CH2-CH3
0.7%	4.2e-12	6		CH3-CH2-CH(ONO2)-CH2-CH2-CH3
0.7%	5.6e-12	7		CH3-CH2-CH(ONO2)-CH2-CH2-CH2-CH3
0.7%	8.5e-12	6		CH3-CH2-CH2-CH2-CH(ONO2)-CH2-OH
0.6%	8.9e-12	4		CH3-CH(OH)-CH(ONO2)-CH3
0.6%	1.9e-11	10		CH3-CH2-CH(OH)-CH2-CH2-CH(ONO2)-CH2-CH2-CH2-CH3
0.6%	1.9e-11	10		CH3-CH2-CH2-CH(OH)-CH2-CH2-CH(ONO2)-CH2-CH2-CH3
0.6%	3.1e-12	6		CH3-C(CH3)(ONO2)-CH(CH3)-CH3
0.6%	1.8e-11	6		CH3-CH(ONO2)-CH2-CH2-CH(OH)-CH2-OH
0.6%	3.4e-12	6		CH3-C(CH3)(OH)-CH2-CH2-CH2-ONO2
0.6%	4.4e-12	6		CH3-CH(ONO2)-CH2-CH2-CH2-CH3
58.0%				All Others

[a] Amount of formation of this compound relative to all products represented as RNO3, on a molar basis.

[b] OH radical rate constant estimated using structure-reactivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996), in units of  $\text{cm}^3 \text{molec}^{-1} \text{sec}^{-1}$ .

[c] Number of carbons.

[d] Detailed model species name used when computing mechanism for compound that was used for deriving the RNO3 mechanism for the model.

[e] Product structure as used in the mechanism generation system. See Section ???. The "\*" symbol is used to indicate groups that are bonded in cyclic compounds. Underlined structures are those used to derive the RNO3 mechanism.



In the case of PROD2, the average OH radical rate constant is  $1.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , and the average carbon number is slightly over 7. For the purpose of deriving a PROD2 mechanism in the model, five individual compounds, indicated by being underlined on Table 3, were chosen as being representative of the entire set. The choice was largely subjective, but was made such that the average OH rate constant and the average number of carbons was approximately the same as the average, and so they included examples of different types of compounds on the list. For each of these five compounds the reaction mechanism with OH and photolysis was generated using the mechanism estimation/generation procedure discussed in Section II.B, and the PROD2 parameters were derived by averaging the values obtained, weighing each of the five compounds equally<sup>3</sup>. Since most of these compounds are ketones, the ketone absorption cross sections and the quantum yields assumed to be appropriate for ketones with 7 carbons (see Section II.B.7.a) were used for the photolysis reactions. The mechanisms derived for these representative individual compounds are included with the mechanism listings for the detailed model species, given in Section ???. Note that although the PROD2 mechanism is derived based on a set of model species with average carbon numbers of 7, this is represented as having 6 carbons in the mechanism for the purpose of computing carbon balance.

In the case of RNO3, the average OH radical rate constant is  $7.8 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , and the average carbon number is around 6.5. The RNO3 mechanism in the model is derived by choosing one representative compound each for carbon numbers of 4-8 and 10, such that the average OH rate constant is close to the average for the mixture. These six compounds are indicated by being underlined on Table 4. The mechanisms for these compounds were generated and the product yield parameters obtained<sup>3</sup> were averaged (weighing each equally) to obtain the product yields for the reactions of RNO3. The rate of photolysis is estimated by using the absorption cross sections given by IUPAC (Atkinson et al, 1997a, 1999) for isopropyl nitrate, assuming unit quantum yield for production for NO<sub>2</sub>.

### c. Uncharacterized Aromatic Ring Fragmentation Products

Despite considerable progress in recent years towards understanding aromatic reaction mechanism (e.g., see Atkinson, 1999, and references therein), there is still insufficient information about the ring-opening products formed with OH radicals react with aromatic compounds to determine the appropriate mechanism for atmospheric modeling. In particular, the observed  $\alpha$ -dicarbonyl and ring-retaining products from the aromatics are insufficient to account for the observed reactivity of aromatics in environmental chamber experiments, and it is necessary to assume formation of products that photolyze relatively rapidly to form radicals for model simulations to fit the environmental chamber data (e.g. Carter, 1990). To fit the data, the Carter (1990) mechanism included model species AFG1 and AFG2 to represent the contribution to reactivity of these uncharacterized ring-fragmentation products, with their yields and approximate photolysis rates adjusted to fit chamber data. Their mechanisms were based roughly on those for glyoxal and methyl glyoxal, respectively, although their action spectrum had a greater short wavelength contribution [eventually being based on that for acrolein (Carter et al, 1993b; Carter, 1995)] in order to fit reactivity data using differing types of light sources. More recently, to fit new aromatics environmental chamber data obtained using Teflon chambers with a xenon arc light source, it was found that it was also necessary to represent at least portion of the uncharacterized ring-opening products by model species with  $\alpha$ -dicarbonyl action spectra (Carter et al, 1997a). These were represented in the model by methyl glyoxal – i.e., by increasing the methyl glyoxal yield by an adjustable amount in order to fit the chamber data (Carter et al, 1997a).

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<sup>3</sup> The mechanisms derived for these representative individual compounds are included with the mechanism listings for the detailed model species, given in Section II.D. The detailed model species names assigned to them are indicated on Table 3 or Table 4.

In this version of the mechanism, the general approach of using photoreactive model species with yields adjusted to fit the chamber data to represent the effects of unknown reactive aromatic ring fragmentation products is retained. However, the number of model species used for this purpose was increased to three, and their mechanisms were derived to be somewhat more consistent with the actual types of species expected to be involved. However, the mechanisms of the model species used were changed to be more consistent with the actual types of unsaturated dicarbonyl species expected to be involved, with their names being changed from AFGn to DCBn. A third model species (DCB3) was added to allow for separate representation of products with action spectra like  $\alpha$ -dicarbonyls, and thus end the use the methyl glyoxal model species (MGLY) for this purpose. This was done so that the mechanism used may be more appropriate for an unsaturated carbonyl, and so model predictions of MGLY will actually represent methyl glyoxal and similar species. These are discussed in more detail below<sup>4</sup>.

DCB1 is used to represent the uncharacterized ring-opening products that do not undergo significant photodecomposition to form radicals. This includes not only the ring fragmentation formed from benzene and naphthalene, but also unsaturated diketones such as 3-hexene-2,5-dione, which the data of Bierbach et al (1994) and Tuazon et al (??) do not undergo significant radical-forming photodecomposition. This non-photoreactive model species replaces the AFG1 used in the previous versions of the mechanism to represent the uncharacterized ring-fragmentation products from benzene because fits to the benzene - NO<sub>x</sub> chamber data are not significantly improved if it is assumed that there are other photoreactive ring-opening products besides glyoxal. This is contrast with the previous version of the mechanism, where significant photolysis of AFG1 to radicals had to be assumed to fit these data. This change is because benzene also forms glyoxal, whose photolysis to radicals was increased significantly in this version of the mechanism in order to be consistent with new chamber data on the reactivity of acetylene (Carter et al, 1997c). Also, the reaction of this species with O<sub>3</sub> is an additional radical source that was not in the previous mechanism.

This species is also used in the mechanisms of the alkylbenzenes because at least some of the ring-opening products are expected to have low photoreactivity, yet are expected to react rapidly by other means, particularly with OH. In particular, o-substituted aromatics such as o-xylene and 1,2,4-trimethylbenzene are expected to form higher yields of unsaturated diketones, which as indicated above do not seem to be highly photoreactive (Bierbach et al, 1994; Tuazon et al, ??). The fact that these o-substituted aromatics have relatively low reactivity in environmental chamber experiments, and that lower yields photoreactive products that give best fits to these data (Carter et al, 1997a), is consistent with the expected lower photoreactivity of these compounds. As discussed in Section II.C.1, the yield of DCB1 is determined by assuming that the sum of all the DCBs (DCB1 + DCB2 + DCB3) is equal to the total ring fragmentation route, where the yields of the photoreactive DCB1 and DCB2 being determined by optimization. Note that this means the DCBs are used represent co-products formed with the measured  $\alpha$ -dicarbonyls, as well as products formed in non- $\alpha$ -dicarbonyl-forming fragmentation routes.

The DCB1 reactions are based roughly on those estimated for HCOCH=CHCHO, with OH and O<sub>3</sub> rate constants based on the data of Bierbach et al (1994), and the mechanisms derived as discussed in Footnotes to Table 46 in Table 47. Although an OH reaction mechanism for an unsaturated diketone product such as might be formed from o-substituted aromatics may be somewhat different than that expected for 2-butene 1,4-dial, best fits to the p-xylene and 1,2,4-trimethylbenzene chamber data are obtained if the present DCB1 + OH mechanism is used.

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<sup>4</sup> See also Section II.C.1 for a discussion of the derivations of the yields and photolysis rates of these species based on model simulations of the aromatic - NO<sub>x</sub> chamber experiments.

DCB2 and DCB3 are used to represent the highly photoreactive ring-opening products formed from alkylbenzenes. As discussed by Carter et al (1997a), to fit chamber data using various light sources, it is necessary to assume two separate model species for this purpose, one with an action spectrum like acrolein, and the other with an action spectrum like an  $\alpha$ -dicarbonyl. DCB2 is used to represent those compounds with action spectra like  $\alpha$ -dicarbonyls, and thus uses absorption cross sections of methyl glyoxal, with a wavelength-independent overall quantum yield adjusted to give best fits to the chamber data as discussed in Section II.C.1. Likewise, DCB3 uses the absorption cross sections of acrolein, with the overall quantum yield adjusted to fit the same chamber data. Note that the overall “quantum yield” used in the model for DCB3 is greater than unity, indicating that the absorption cross sections of the actual compounds being represented must be significantly greater than those for acrolein. However, in view of lack of information concerning the nature of these compounds and their photolysis reactions, it is assumed that the wavelength dependence of the action spectra are approximately the same as that for acrolein.

Other than the photolysis rates, the reactions of DCB2 and DCB3 are the same. They are based roughly on estimated mechanisms for  $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CHCHO}$ . The rate constant for the OH reaction was assumed to be the same as that used for DCB1, with the mechanism estimated as indicated in footnotes to Table 46 in Table 47. Because of the rapid photolysis, it is assumed that consumption of these species by reaction with  $\text{O}_3$  is negligible. The photolysis mechanisms are unknown, and are probably highly variable depending on the individual species involved. In this mechanism, these are very approximately represented by an estimated set of products is used which gives reasonably good performance in model simulations of available chamber data (see Section II.C.1).

#### **d. Unreactive Product Species**

The mechanism has several model species whose subsequent reactions are ignored, either because they are unreactive or because the effects of their gas-phase reactions are expected to be small. These also include “counter species” for the purpose of tracking carbon and nitrogen balance. Since their computed concentrations do not effect transformations of any of the other gas-phase species, they could be eliminated from the model if their concentrations, or tracking carbon or nitrogen balance, are not of interest.

Formic Acid ( $\text{HCOOH}$ ), Acetic Acid ( $\text{CCO-OH}$ ), Lumped Higher Organic Acids ( $\text{RCO-OH}$ ), Peroxy Acetic Acid ( $\text{CCO-OOH}$ ), and Lumped Higher Organic Peroxy Acids ( $\text{RCO-OOH}$ ). Formic acid is predicted to be formed in the reactions of formaldehyde with  $\text{HO}_2$ , acetic and higher organic acids are predicted to be formed from the reactions of acyl peroxy radicals with other peroxy radicals, and peroxy acetic and higher peroxy acids are predicted to be formed when acyl peroxy radicals react with  $\text{HO}_2$ . In addition, formation of formic and higher organic acids are assumed to be the major fate of stabilized Crigiee biradicals (Atkinson, 1997a, 1999). Their subsequent reactions with OH radicals is assumed to be negligible compared to other loss processes such as deposition, though the reaction with OH may in fact be non-negligible for the higher acids or peroxy acids. Formation of these acids is included in the model because of their potential involvement in acid deposition. Depending on the model application, it may be appropriate to remove them from the model or lump them into a single organic acid species.

Carbon Dioxide ( $\text{CO}_2$ ). Since  $\text{CO}_2$  does not undergo gas-phase reactions and its formation is not expected to have any other effects on the environment (since background  $\text{CO}_2$  concentrations are much higher), the only reason for having this species in the model is carbon balance.

Unreactive Carbon (NROG). This model species is used to represent emitted VOCs or VOC oxidation products whose subsequent reactions are assumed to be negligible, and which are not otherwise represented in the model. It can be removed from the model if carbon balance is not of interest. It is represented as having one carbon, with the other carbons in the unreactive VOC or product being represented by the “lost carbon” species.

Lost Carbon (XC). The lost carbon model species is used to account for carbons that are lost (or gained) if the model species has a different number of carbons than the VOC or VOC products being represented. Note that this is different from the “unreactive carbon” (NROG) model species in that the former is used to represent *molecules* that are treated as unreactive, while the latter represents *parts of molecules* that are not being represented (i.e., that are “lost”) as a result of the mechanism condensation processes. This model species can be removed in model applications where carbon balance is not of interest.

Lost Nitrogen (XN). This model species is analogous to the lost carbon (XC) species except that in this case it is used for nitrogen balance. It is not recommended that this be removed from the mechanism, so that nitrogen balance can always be verified in any model simulation. Because of the importance of nitrogen species in affecting not only O<sub>3</sub> formation but also radical cycles and chain lengths, any modeling system that does not maintain proper nitrogen balance must be considered to be unreliable.

Hydrogen (H2). The mechanism includes the formation of H<sub>2</sub> from the photolysis of formaldehyde, but the subsequent reaction of H<sub>2</sub> with OH is ignored because of the low rate constant and the relatively small amount formed. Tracking H<sub>2</sub> in the model is useful only for mechanism evaluation studies if instrumentation to measure H<sub>2</sub> is available, and can be eliminated from the model for ambient simulations or other applications.

Sulfates (SULF). The SULF model species is used to represent the formation of SO<sub>3</sub> from the reactions of SO<sub>2</sub> with OH. It is assumed that the fate of SO<sub>3</sub> in the atmosphere would be formation of sulfate aerosol. This model species would be important in models for secondary aerosol formation in scenarios where SO<sub>2</sub> is emitted, but could be removed if aerosols are not represented in the model application.

## **B. Generated and Estimated Mechanisms**

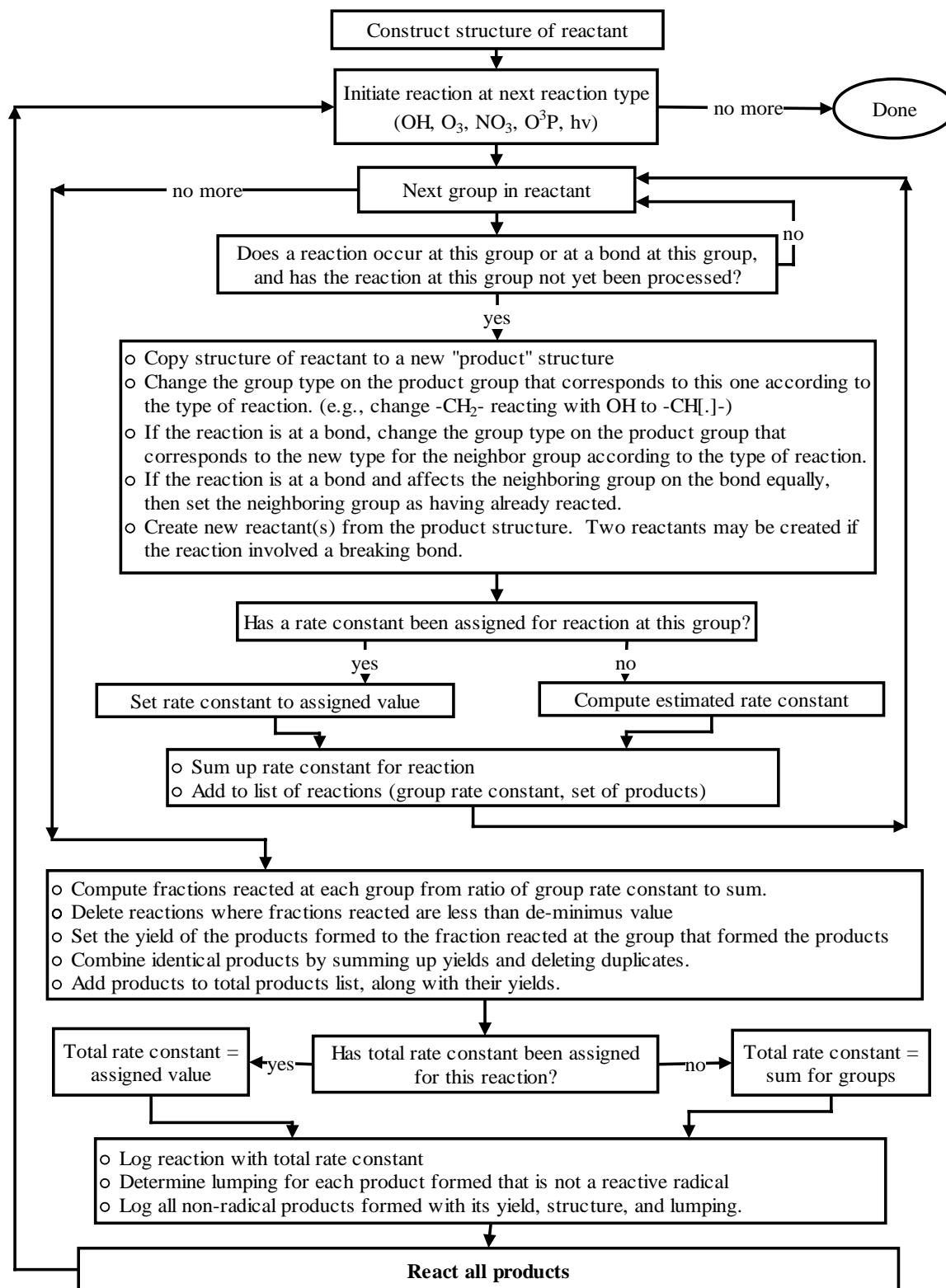
The atmospheric reaction mechanisms for most of the organic compounds that are represented by this mechanism are complex, can involve a large number of reactive intermediates (particularly for larger molecules), and in almost all cases involve reactions whose rate constants are unknown and have to be estimated. Because of the complexity, for practical reasons it is necessary either to greatly simplify the mechanisms for most VOCs, use extensive lumping or condensations in VOC representations, or use an automated procedure to generate the mechanisms. In the previous versions of the SAPRC mechanism, an automated procedure was used to derive mechanisms for the alkanes, but molecule-by-molecule assignments or various lumping or condensation approaches were used for all the other VOCs. In this version, an automated procedure is now used to derive the mechanisms for a much wider variety of compounds, which includes almost all compounds for which mechanistic assignments have been made except for the aromatics and terpenes. This procedures, estimation methods, and assignments that it employs are discussed in this section.

## 1. Mechanism Generation Procedure Overview

The mechanism generation is carried out using a set of object-oriented computer programs that derives explicit mechanisms for the major atmospherically-relevant reactions of a VOC in the presence of  $\text{NO}_x$ , given the structure of the VOC. The results are then used to determine the representation of these reactions in terms of the model species in the base mechanism. The current system can generate the atmospherically-relevant reactions of alkanes, monoalkenes, a variety of oxygenates, and selected dialkenes and alkynes with OH, reactions of monoalkenes and selected dialkenes with  $\text{O}_3$ ,  $\text{NO}_3$ , and  $\text{O}^3\text{P}$ , and photolysis reactions of carbonyls and organic nitrates. The overall operation of the system involves the following steps:

- The user inputs the structure of the compound. The structure is specified in terms of “groups” such as  $-\text{CH}_2-$ ,  $-\text{CO}-$ ,  $-\text{OH}$ , etc., which are similar to those used in the group additivity thermochemical estimation methods of Benson (1976) or the structure-reactivity kinetic estimate methods of Atkinson (1987). The specific groups used are summarized in Section II.B.2.
- The initial reactions of the compound with OH,  $\text{O}_3$ ,  $\text{NO}_3$ ,  $\text{O}^3\text{P}$  or photolysis are processed as shown schematically on Figure 1. The rates of reactions at competing positions are estimated as discussed in Sections II.B.3 through II.B.6.d, and the products and radicals formed, together with their yields, are logged. Documentation text is generated and logged, as appropriate.

Figure 1. Flow diagram for the initial reactions of a VOC in the mechanism generation process.



- For each reactive organic radical formed, either in the initial reaction with OH, etc., or through the reactions of a previously formed radical, the system generates all the reactions that are believed to be potentially important for the radical in the presence of NO<sub>x</sub> in air. The radicals and products formed, and their yields (obtained by multiplying the yield of the starting radical times the branching ratios for the reactions forming them) are logged for further processing. Documentation text is also generated and logged for those reactions where estimates are involved. The types of radicals involved, and the reactions the system considers, are as follows:
  - Carbon centered (e.g. alkyl) radicals: Reaction with O<sub>2</sub>. In most cases this involves formation of the corresponding peroxy radical, but in a few cases (e.g. α-hydroxy alkyl radicals) other reactions can occur. In all cases, only a single reaction pathway is assumed, so the yield of the product(s) are assigned the yield of the starting radical. These reactions are discussed in Section II.B.8.
  - Peroxy radicals (other than acetyl peroxy): Reaction with NO. This can involve formation of the corresponding alkyl nitrate (RONO<sub>2</sub>) or formation of NO<sub>2</sub> and the corresponding alkoxy (RO·) radical. The conversion of NO to NO<sub>2</sub> in the latter reaction is logged as the formation of the “NO to NO<sub>2</sub> conversion product”. Nitrate yield estimates, discussed in Section II.B.9, are used to determine the yields of the nitrate, alkoxy radical, and NO to NO<sub>2</sub> conversion products relative to the starting radical.
  - Alkoxy radicals: Reaction with O<sub>2</sub>; β-scission decomposition; 1,4-H shift isomerization; or α-ester rearrangement (Tuazon et al, 1998b), when possible. The O<sub>2</sub> reaction involves the formation of HO<sub>2</sub> and a stable product, while the other reactions can involve formation of various carbon-centered radicals, in some cases with stable co-products. Various estimation methods or assignments, discussed in Section II.B.10 are used to derive the relevant rate constants or branching ratios.

Note that acetyl peroxy radicals (e.g. RC(O)O<sub>2</sub>·) are treated as product species and their reactions are not generated. This is because they are lumped with generic acyl peroxy radical species in the model (e.g., CCO-O<sub>2</sub>· or RCO-O<sub>2</sub>·), so the information obtained by generating their reactions is not used. Note that their ultimate products they form depend (PAN or RC(O)O· decomposition products) depend on environmental conditions and thus cannot be uniquely determined.

- For each “product” species formed, which includes acetyl peroxy radicals, HO<sub>2</sub> and the NO to NO<sub>2</sub> conversion product as well as stable organic products, the yield, structure, and generation (number of NO to NO<sub>2</sub> conversions involved before it is formed) is logged. The lumping assignment for the product (the way it is represented in the base mechanism) is also determined and logged. Lumping assignments are discussed in Section 0.
- Processing is completed once all the reactive radicals have been converted to stable products or radicals whose reactions are not generated (e.g., HO<sub>2</sub> or acyl peroxy radicals). The generated reaction list, product log (list of all products giving yields, structure and lumping), is saved for output or processing.
- Once all the relevant reactions for a VOC have been generated, the overall reactions or mechanistic parameters for the species can be derived, for use in model simulations. The sum of the yields of HO<sub>2</sub> and the NO to NO<sub>2</sub> conversion product in the product log are used to derive the corresponding HO<sub>2</sub>, RO<sub>2</sub>-R· and/or R<sub>2</sub>O<sub>2</sub>· yields. The yields of the lumped species representing the various organic products are summed to determine their total yields in the overall reaction. Loss or gain of carbon and nitrogens are tracked, and if necessary yields of “lost carbon” or “lost nitrogen” model species are determined to maintain balance.

Note that the system does not generate complete mechanisms for the VOCs, since peroxy + peroxy and peroxy + NO<sub>2</sub> reactions are ignored, and as indicated above acetyl peroxy radical reactions are not generated. However, even if the system generated all the peroxy + peroxy reactions, the current mechanism is not set up to use this information, because of the way the reactions of peroxy radicals are represented (see Section II.A.2.d). The present mechanism neglects the formation and decompositions of most peroxy nitrates because their rapid decompositions at ambient temperatures result in no net reaction, so information on the formation and generation of these species would also be ignored. The current mechanism is also not set up to take advantage of any detailed product information concerning the reactions of individual acyl peroxy radicals and their corresponding PAN analogues. Therefore the present system is sufficient to provide all the information that the current version of the mechanism can use. Expanded capabilities can be added in the future as mechanisms and models that can use them are developed.

## **2. Specification of Reactants and Summary of Groups**

In this section, the method used to specify structures of reactions, and the types of structures that can be represented, are discussed. A knowledge of this is necessary not only for those who wish to use the system, but also because some of the tables given in this report use this method to identify reactants and radicals.

The structure of a reactant VOC or radical is specified by giving the “groups” in the molecule, and indicating which groups they are bonded to. Groups are parts of the molecule that are treated as a unit by the system, and as indicated above are generally the same as the groups used in the structure-reactivity kinetic estimation method of Atkinson and co-workers (Atkinson, 1987; Kwok and Atkinson, 1995; Atkinson, 1997a). The list of groups that can be supported by the present system is given in Table 5 and Table 6. Table 5 shows the groups that can be used for constructing VOC structures to be reacted with OH, etc, and Table 6 shows the groups that can appear in reactive radical and product species that are formed.

If the molecule or radical contains atoms not shown on Table 5 or Table 6, then the reactions of that species cannot be generated by the current system. In addition, there are some groups for which there are insufficient thermochemical group additivity data in the system’s thermochemical database to support the data requirements of the estimation methods, which means that reactions of molecules containing those groups usually cannot be generated. Those cases are indicated on Table 5.



Table 5. Listing of groups for stable molecules that can be supported by the present mechanism generation system.

Group	Reactions at Group
<u>Groups for which mechanisms can usually be generated</u>	
-CH <sub>3</sub>	OH (H- Abstraction)
-CH <sub>2</sub> -	OH (H- Abstraction)
>CH-	OH (H- Abstraction)
>C<	none
-O-	none
-OH	OH (H- Abstraction)
-CHO	OH, NO <sub>3</sub> (H- Abstraction), hv (HCO..- Bond Scission)
-CO-	hv (CO..- Bond scission)
=CH <sub>2</sub>	OH, O <sub>3</sub> , O <sup>3</sup> P, NO <sub>3</sub> (Double Bond Addition)
=CH	OH, O <sub>3</sub> , O <sup>3</sup> P, NO <sub>3</sub> (Double Bond Addition)
=C<	OH, O <sub>3</sub> , O <sup>3</sup> P, NO <sub>3</sub> (Double Bond Addition)
<u>Groups for which mechanisms can be generated in some cases</u>	
-ONO <sub>2</sub>	hv (-O. + NO <sub>2</sub> formation)
<u>Groups for which mechanisms usually cannot be generated</u>	
-F	none
-Cl	none
-Br	none
-I	none
-NO <sub>2</sub>	none

Table 6. Listing of radical center groups and non-reactive product groups that can be supported by the present mechanism generation system.

Group	Reactions at Group
<u>Carbon-Centered Radical centers</u>	
CH3.	O2 -> CH3OO.
-CH2.	O2 -> -CH2OO.
-CH[.]-	O2 -> -CH[OO.]
>C[.]-	O2 -> >C[OO.]
HCO.	O2 -> HO2. + CO
-CO.	O2 -> -CO[OO.]
<u>Vinyllic Radical centers</u>	
=CH.	X=CH2 + O2 -> X=O + HCO., where X is =CH2, =CH-, or =C<
=C[.]	X=CH[.] + O2 -> X=O + -C[OO.], where X is =CH2, =CH-, or =C<
<u>Peroxy Radical Centers</u>	
CH3OO.	NO -> CH3O.
-CH2OO.	NO -> -CH2O. + [NO conv NO2], NO -> -CH2-ONO2
-CH[OO.]	NO -> -CH[O.] + [NO conv NO2], NO -> -CH(ONO2)-
>C[OO.]	NO -> >C[O.] + [NO conv NO2], NO -> >C(ONO2)-
<u>Acyl Peroxy Radical Centers</u>	
-CO[OO.]	Not reacted
<u>Alkoxy radical Centers</u>	
CH3O.	O2 -> HO2 + HCHO
-CH2O.	O2 -> HO2 + -CHO, Decomposition, 1,5-H-shift isom, Ester rearrangement
-CH[O.]	O2 -> HO2 + -CO-, Decomposition, 1,5-H shift isom, Ester rearrangement
>C[O.]	Decomposition, 1,5-H shift isom.
HCO2.	O2 -> HO2 + CO2
-CO2.	Decomposition to R. + CO2
<u>Carbene Radical Centers</u>	
CH2:	O2 -> CH2OO[excited]
-CH:	O2 -> -CHOO[excited]
-C[:]-	O2 -> COO[excited]
<u>Excited Crigee Biradical Centers</u>	
CH2OO[excited]	Various unimolecular reactions -- see text
-CHOO[excited]	Various unimolecular reactions -- see text
-COO[excited]-	Various unimolecular reactions -- see text
<u>Stabilized Crigee Biradical Centers</u>	
CH2OO[stab]	Not reacted
-CHOO[stab]	Not reacted
-COO[stab]-	Not reacted
<u>Elementary Product Groups</u>	
CH4	Not reacted (elementary product)
HCHO	Not reacted (elementary product)
CO	Not reacted (elementary product)
CO2	Not reacted (elementary product)
NO2	Not reacted (elementary product)
[NO conv NO2]	Used for Mechanism Processing

The structures of the molecules are specified as follows. Straight chain structures are given by groups separated by "-" or "=". For example:

Propane:	CH3-CH2-CH3
Propionic acid:	CH3-CH2-CO-OH
Ethyl acetate:	CH3-CH2-O-CO-CH3
ethoxyethanol:	HO-CH2-CH2-O-CH2-CH2-O-CH2-CH2-OH

Branched structures are indicated by using ()'s to show groups off to the side. For example:

Isobutane:	CH3-CH(CH3)-CH3
3,3-diethyl pentan-2-ol:	CH3-CH(OH)-C(CH2-CH3)(CH2-CH3)-CH2-CH3
4-isopropyl heptane:	CH3-CH2-CH2-CH(CH(CH3)-CH3)-CH2-CH2-CH3

Cyclic structures are indicated by using a "\*" character to mark the group which is used to close the ring. Note that the present system does not support specification of compounds with more than one ring, since no way of indicating such structures is presently defined.

3-methyl furan: \*O-CH2-CH(CH3)-CH2-CH2-\*

The system presently supports structures with single double bonds between carbon-centered groups only, and may not successfully generate reactions for non-hydrocarbon species with double bonds because of insufficient thermochemical group data in the present database. Double bonds are indicated using a "=" symbol in place of a "-", and *cis* and *trans* configurations are indicated using parentheses, as follows:

<i>cis</i> -2-butene:	CH3-CH=CH-CH3
<i>trans</i> -2-Hexene:	CH3-CH=CH(CH2-CH2-CH3)

Although one can often enter structures in more than one way (for example, both CH3-CH(CH3)-CH2-CH3 and CH3-CH2-CH(CH3)-CH3 are acceptable ways to enter 2-methyl butane), the system uses an algorithm to generate a (usually) unique structure definition string for each structure. This is done so that the structure definition string can be used to determine if two products or intermediate species generated by the system are the same compound. Therefore, the structure specification generated by the system when a new molecule is specified may be slightly different than the one input by the user, though they would refer to the same compound. Note that the current version of the software is not completely finished in this regard, since unique structure definition strings are not always produced for some cyclic compounds. However, this only causes inefficiency in the mechanism generation algorithm, not errors in the generation of the reactions.

In order for the system to be useful for generating mechanisms for a wider variety of compounds, it is also possible to specify *special reactants* whose structures cannot be specified explicitly. Although the system cannot automatically generate reactions for these special reactants, it will accept assignments for their reactions. If these assigned reactions form products that can be specified with known groups, the system then automatically generate the reactions of these products, thus generating the overall reaction mechanism of the special reactant. The special reactants that are supported in the present system are listed in Table 7

Table 7. Special reactants that are presently supported as reactants or products in the mechanism generation system

Reactant	Designation	Reactions Supported
1,3-Butadiene	CH <sub>2</sub> =CH-CH=CH <sub>2</sub>	OH, O <sub>3</sub> , O <sup>3</sup> P, NO <sub>3</sub> (Double Bond Addition)
Isoprene	CH <sub>2</sub> =CH-C(CH <sub>3</sub> )=CH <sub>2</sub>	OH, O <sub>3</sub> , O <sup>3</sup> P, NO <sub>3</sub> (Double Bond Addition)
Acetylene	HC::CH	OH, O <sub>3</sub>
Methyl Acetylene	HC::C-CH <sub>3</sub>	OH, O <sub>3</sub>
1-Butyne	HC::C-CH <sub>2</sub> -CH <sub>3</sub>	OH, O <sub>3</sub>
2-Butyne	CH <sub>3</sub> -C::C-CH <sub>3</sub>	OH, O <sub>3</sub>
3-Methyl Furan	*O-CH=C(CH <sub>3</sub> )-CH=CH-*	Product only (formed from isoprene)

### 3. Reactions with OH Radicals

Reactions with OH radicals can occur by two mechanisms, depending on whether the group has a double bond or an abstractable hydrogen. If the group has an abstractable hydrogen, the reaction is



where XH is any H-containing group and X· is the corresponding depending on whether the compound. If the group has a double bond, the reaction is



Note that two reactions are generated for each double bond, one where the OH adds to each side of the bond. (If the reactions are equivalent, as would be the case for symmetrical molecules, they are combined after they are generated – the system uses the products formed to determine equivalency.) For each molecule that reacts with OH, one reaction is generated for each group in the molecule that can react in this way. The fractions reacted at the various group are determined from the ratio of the estimated rate constant at each group, divided by the total of the estimated rate constants for all groups. The group rate constants are estimated as discussed below.

#### a. Assigned Total OH Radical Rate Constants

Total OH radical rate constants have been measured for many (indeed most) of the VOCs in the current mechanism, and in those cases assigned rate constants are used when generating the mechanisms rather than estimated values. Table 8 gives the OH radical rate constants assigned to all VOCs in the current mechanism, along with references and notes indicating the basis for the assignment. Most of the rate constants are based on recommendations by Atkinson (1989, 1994, 1997a). For completeness, this table has the rate constants for all VOCs in the current mechanism for which such assignments have been made, including those (e.g., aromatics and terpenes) whose mechanisms cannot be generated by the current system. For VOCs whose OH reactions can be automatically generated by the system, the table also shows the estimated T=300K rate constants, which were derived as discussed in the following section. The percentage differences between the assigned and estimated values are also shown.

Table 8. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with OH radicals in the present mechanism.

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
<u>Alkanes</u>								
Ethane	ETHANE	2.60e-13	1.37e-12	2.0	0.990	1	2.78e-13	7%
Propane	PROPANE	1.14e-12	1.40e-12	2.0	0.121	1	1.28e-12	12%
n-Butane	N-C4	2.47e-12	1.52e-12	2.0	-0.288	1	2.65e-12	7%
n-Pentane	N-C5	4.04e-12	2.20e-12	2.0	-0.364	1	4.07e-12	1%
n-Hexane	N-C6	5.47e-12	1.38e-12	2.0	-0.823	1	5.49e-12	0%
n-Heptane	N-C7	7.04e-12	1.43e-12	2.0	-0.950	1	6.91e-12	-2%
n-Octane	N-C8	8.76e-12	2.48e-12	2.0	-0.751	1	8.33e-12	-5%
n-Nonane	N-C9	1.00e-11	2.26e-12	2.0	-0.888	1	9.75e-12	-3%
n-Decane	N-C10	1.13e-11	2.82e-12	2.0	-0.827	1	1.12e-11	-1%
n-Undecane	N-C11	1.29e-11				1	1.26e-11	-2%
n-Dodecane	N-C12	1.39e-11				1	1.40e-11	1%
n-Tridecane	N-C13	1.60e-11				1	1.54e-11	-4%
n-Tetradecane	N-C14	1.80e-11				1	1.69e-11	-6%
n-Pentadecane	N-C15	2.10e-11				1	1.83e-11	-13%
n-C16	N-C16	2.30e-11				1	1.97e-11	-14%
Isobutane	2-ME-C3	2.21e-12	1.04e-12	2.0	-0.447	1	2.45e-12	11%
Iso-Pentane	2-ME-C4	3.70e-12				1	4.05e-12	9%
Neopentane	22-DM-C3	8.63e-13	1.62e-12	2.0	0.376	1	6.83e-13	-21%
2-Methyl Pentane	2-ME-C5	5.30e-12				1	5.47e-12	3%
3-Methylpentane	3-ME-C5	5.40e-12				1	5.75e-12	6%
2,3-Dimethyl Butane	23-DM-C4	5.79e-12	1.12e-12	2.0	-0.982	1	5.45e-12	-6%
2,2-Dimethyl Butane	22-DM-C4	2.38e-12	3.22e-11		1.552	1	1.84e-12	-23%
2,2-Dimethyl Pentane	22-DM-C5	3.40e-12				1	3.26e-12	-4%
2,4-Dimethyl Pentane	24-DM-C5	5.00e-12				1	6.87e-12	37%
2,2,3-Trimethyl Butane	223TM-C4	4.25e-12	7.61e-13	2.0	-1.025	1	3.24e-12	-24%
2,2,3,3-Tetrame. Butane	2233M-C4	1.06e-12	1.72e-12	2.0	0.286	1	1.02e-12	-4%
2,2,4-Trimethyl Pentane	224TM-C5	3.60e-12	1.87e-12	2.0	-0.389	1	4.66e-12	30%
2,3,4-Trimethyl Pentane	234TM-C5	7.10e-12				1	8.55e-12	20%
2,2-Dimethyl Hexane	22-DM-C6	4.80e-12				1	4.68e-12	-2%
2,3,5-Trimethyl Hexane	235TM-C6	7.90e-12				1	9.97e-12	26%
3,3-Diethyl Pentane	33-DE-C5	4.90e-12				1	5.31e-12	8%
2-Methyl Octane	2-ME-C8	1.01e-11				1	9.73e-12	-4%
4-Methyl Octane	4-ME-C8	9.70e-12				1	1.00e-11	3%
3,4-Diethyl Hexane	34-DE-C6	7.40e-12				1a	1.25e-11	69%
2-Methyl Nonane	2-ME-C9	1.28e-11				1b	1.12e-11	-12%
2,6-Dimethyl Octane	26DM-C8	1.29e-11				1b	1.14e-11	-12%
Cyclopropane	CYCC3	8.40e-14				1	8.52e-14	1%
Cyclobutane	CYCC4	1.50e-12				1	1.59e-12	6%
Cyclopentane	CYCC5	5.06e-12	2.31e-12	2.0	-0.467	1	4.54e-12	-10%
Isopropyl Cyclopropane	IPR-CC3	2.70e-12				1	2.86e-12	6%
Cyclohexane	CYCC6	7.26e-12	2.59e-12	2.0	-0.614	1	8.52e-12	17%
Cycloheptane	CYCC7	1.30e-11				1	9.94e-12	-24%

Table 8 (continued)

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
Methylcyclohexane	ME-CYCC6	1.00e-11				1	1.02e-11	2%
Cyclooctane	CYCC8	1.40e-11				1	1.14e-11	-19%
1,1,3-Trimethyl Cyclohex.	113MCYC6	8.70e-12				1	9.12e-12	5%
Hexyl Cyclohexane	C6-CYCC6	1.78e-11				2	1.77e-11	-1%
<u>Alkenes</u>								
Ethene	ETHENE	8.43e-12	1.96e-12		-0.870	1	8.44e-12	0%
Propene	PROPENE	2.60e-11	4.85e-12		-1.002	1	3.16e-11	21%
1-Butene	1-BUTENE	3.11e-11	6.55e-12		-0.928	1	3.16e-11	2%
3-Methyl-1-Butene	3M-1-BUT	3.14e-11	5.32e-12		-1.059	1	3.16e-11	1%
1-Pentene	1-PENTEN	3.11e-11	5.86e-12		-0.994	13	3.16e-11	2%
1-Hexene	1-HEXENE	3.66e-11	6.91e-12		-0.994	13	3.16e-11	-14%
3,3-Dimethyl-1-Butene	33M1-BUT	2.77e-11	5.23e-12		-0.994	13	3.16e-11	14%
1-Heptene	1-HEPTEN	3.96e-11	7.47e-12		-0.994	13	3.16e-11	-20%
Isobutene	ISOBUTEN	5.09e-11	9.47e-12		-1.002	1	5.79e-11	14%
2-Methyl-1-Butene	2M-1-BUT	6.04e-11	1.14e-11		-0.994	13	5.79e-11	-4%
2-Methyl-1-Pentene	2M1-C5E	6.23e-11	1.18e-11		-0.994	13	5.79e-11	-7%
trans-2-Butene	T-2-BUTE	6.32e-11	1.01e-11		-1.093	1	6.34e-11	0%
cis-2-Butene	C-2-BUTE	5.58e-11	1.10e-11		-0.968	1	6.34e-11	14%
2-Methyl-2-Butene	2M-2-BUT	8.60e-11	1.92e-11		-0.894	1	8.71e-11	1%
trans-2-Pentene	T-2-PENT	6.63e-11	1.25e-11		-0.994	13	6.34e-11	-4%
cis-2-Pentene	C-2-PENT	6.43e-11	1.21e-11		-0.994	13	6.34e-11	-1%
2,3-Dimethyl-2-Butene	23M2-BUT	1.09e-10	2.05e-11		-0.994	13	1.05e-10	-4%
Trans 4-Methyl-2-Hexene	T4M2-C5E	6.04e-11	1.14e-11		-0.994	13	6.34e-11	5%
2-Methyl-2-Pentene	2M-2-C5E	8.81e-11	1.66e-11		-0.994	13	8.71e-11	-1%
2,3-Dimethyl-2-Hexene	23M2-C5E	1.02e-10	1.92e-11		-0.994	13	1.05e-10	3%
Trans 4,4-dimethyl-2-Hexene	T44M2C5E	5.44e-11	1.03e-11		-0.994	13	6.34e-11	16%
Trans-2-Heptene	T-2-C7E	6.73e-11	1.27e-11		-0.994	13	6.34e-11	-6%
Trans-4-Octene	T-4-C8E	6.83e-11	1.29e-11		-0.994	13	6.34e-11	-7%
Cyclopentene	CYC-PNTE	6.63e-11	1.25e-11		-0.994	13	6.34e-11	-4%
Cyclohexene	CYC-HEXE	6.70e-11	1.26e-11		-0.994	13	6.34e-11	-5%
1,3-Butadiene	13-BUTDE	6.59e-11	1.48e-11		-0.890	1		
Isoprene	ISOPRENE	1.00e-10	2.55e-11		-0.815	1		
3-Carene	3-CARENE	8.71e-11	1.64e-11		-0.994	13		
Sabinene	SABINENE	1.16e-10	2.19e-11		-0.994	13		
b-Pinene	B-PINENE	7.82e-11	2.38e-11		-0.709	1		
d-Limonene	D-LIMONE	1.69e-10	3.19e-11		-0.994	13		
a-Pinene	A-PINENE	5.31e-11	1.21e-11		-0.882	1		
Styrene	STYRENE	5.80e-11				1		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	3.16e-11				1		
<u>Aromatics</u>								
Benzene	BENZENE	1.24e-12	2.47e-12		0.411	3		
Toluene	TOLUENE	5.91e-12	1.81e-12		-0.705	3		

Table 8 (continued)

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
Ethyl Benzene	C2-BENZ	7.10e-12				3		
n-Propyl Benzene	N-C3-BEN	6.00e-12				3		
Isopropyl Benzene (cumene)	I-C3-BEN	6.50e-12				3		
s-Butyl Benzene	S-C4-BEN	6.00e-12				10		
m-Xylene	M-XYLENE	2.36e-11	2.36e-11		0.000	3		
o-Xylene	O-XYLENE	1.37e-11	1.37e-11		0.000	3		
p-Xylene	P-XYLENE	1.43e-11	1.43e-11		0.000	3		
1,2,4-Trimethyl Benzene	124-TMB	3.25e-11	3.25e-11		0.000	3		
1,3,5-Trimethyl Benzene	135-TMB	5.75e-11	5.75e-11		0.000	3		
1,2,3-Trimethyl Benzene	123-TMB	3.27e-11	3.27e-11		0.000	3		
Indan	INDAN	9.20e-12				12		
Naphthalene	NAPHTHAL	2.12e-11	1.07e-12		-1.779	3		
Tetralin	TETRALIN	3.43e-11				6		
1-Methyl Naphthalene	1ME-NAPH	5.30e-11				11		
2-Methyl Naphthalene	2ME-NAPH	5.23e-11				5		
Methyl Naphthalenes	ME-NAPH	5.20e-11				4		
2,3-Dimethyl Naphth.	23-DMN	7.68e-11				5		
Phenol	PHENOL	2.63e-11				3		
o-Cresol	O-CRESOL	4.20e-11				3		
m-Cresol	M-CRESOL	6.40e-11				3		
p-Cresol	P-CRESOL	4.70e-11				3		
Nitrobenzene	NO2-BENZ	1.50e-13				8		
Monochlorobenzene	CL-BEN	7.70e-13				3		
p-Dichlorobenzene	CL2-BEN	5.55e-13				7		
Benzotrifluoride	CF3-BEN	4.60e-13				9		
p-Trifluoromethyl-Cl-Benzene	PCBTf	2.40e-13				9		
<u>Alkynes</u>								
Acetylene	ACETYLEN	9.12e-13	9.40e-12		1.391	14		
Methyl Acetylene	ME-ACTYL	5.90e-12				14		
Ethyl Acetylene	ET-ACTYL	8.00e-12				14		
2-Butyne	2-BUTYNE	2.72e-11	1.00e-11		-0.596	14		
<u>Alcohols and Glycols</u>								
Methanol	MEOH	9.34e-13	3.10e-12		0.715	17	6.25e-13	-33%
Ethanol	ETOH	3.28e-12	5.56e-13		-1.057	17	3.61e-12	10%
Isopropyl Alcohol	I-C3-OH	5.32e-12	6.49e-13		-1.254	14	7.26e-12	37%
n-Propyl Alcohol	N-C3-OH	5.53e-12				14	5.51e-12	0%
t-Butyl Alcohol	T-C4-OH	1.13e-12	3.86e-13		-0.640	21	6.87e-13	-39%
n-Butyl Alcohol	N-C4-OH	8.57e-12				14	6.93e-12	-19%
Cyclopentanol	CC5-OH	1.07e-11				22	1.03e-11	-4%
Pentyl Alcohol	C5OH	1.11e-11				14	8.35e-12	-25%
2-Pentanol	2-C5OH	1.18e-11				22	1.14e-11	-3%
3-Pentanol	3-C5OH	1.22e-11				22	1.30e-11	7%

Table 8 (continued)

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
2-Hexanol	2-C6OH	1.21e-11				22	1.28e-11	6%
1-Hexanol	1-C6OH	1.25e-11				14	9.78e-12	-22%
1-Heptanol	1-C7OH	1.37e-11				14	1.12e-11	-18%
1-Octanol	1-C8-OH	2.02e-11				23	1.26e-11	-38%
2-Octanol	2-C8-OH	2.52e-11				23	1.56e-11	-38%
3-Octanol	3-C8-OH	3.14e-11				23	1.73e-11	-45%
4-Octanol	4-C8-OH	2.87e-11				23	1.73e-11	-40%
Ethylene Glycol	ET-GLYCL	1.47e-11				24	8.38e-12	-43%
Propylene Glycol	PR-GLYCL	2.15e-11				24	1.28e-11	-40%
<u>Ethers and Glycol Ethers</u>								
Dimethyl Ether	ME-O-ME	3.01e-12	1.04e-11		0.739	14	2.30e-12	-24%
Trimethylene Oxide	TME-OX	1.03e-11				16	5.76e-12	-44%
Tetrahydrofuran	THF	1.61e-11				14	1.41e-11	-12%
Diethyl Ether	ET-O-ET	1.31e-11	8.02e-13		-1.663	14	1.59e-11	22%
Alpha-Methyltetrahydrofuran	AM-THF	2.20e-11	2.52e-12		-1.292	25	2.08e-11	-5%
Tetrahydropyran	THP	1.38e-11				16	2.34e-11	70%
Methyl n-Butyl Ether	MNBE	1.48e-11				14	1.35e-11	-9%
Methyl t-Butyl Ether	MTBE	2.94e-12	5.89e-13		-0.960	14	1.66e-12	-44%
Ethyl t-Butyl Ether	ETBE	8.84e-12				14	8.48e-12	-4%
Di n-Propyl Ether	PR-O-PR	1.84e-11	1.18e-12		-1.639	14	2.18e-11	18%
Ethyl n-Butyl Ether	ENBE	2.13e-11				14	2.03e-11	-5%
Methyl t-Amyl Ether	MTAE	7.91e-12				22	2.82e-12	-64%
Di-n-butyl Ether	BU-O-BU	2.88e-11				14	2.46e-11	-15%
Di-Isobutyl Ether	IBU2-O	2.60e-11				26	2.46e-11	-5%
Di-n-Pentyl Ether	C5-O-C5	3.47e-11				27	2.75e-11	-21%
2-Methoxy-Ethanol	MEO-ETOH	1.33e-11	4.50e-12		-0.646	16	1.49e-11	12%
1-Methoxy-2-Propanol	MEOC3OH	2.00e-11				29	1.93e-11	-3%
2-Ethoxy-Ethanol	ETO-ETOH	1.87e-11				28	2.17e-11	16%
3-Ethoxy-1-Propanol	3ETOC3OH	2.20e-11				16	2.31e-11	5%
3-Methoxy-1-Butanol	3MEOC4OH	2.36e-11				16	2.67e-11	13%
2-Butoxy-Ethanol	BUO-ETOH	2.57e-11				30	2.61e-11	2%
2-(2-Ethoxyethoxy) EtOH	CARBITOL	5.08e-11				31	4.09e-11	-19%
<u>Esters</u>								
Methyl Formate	ME-FORM	2.27e-13				32	1.25e-13	-45%
Ethyl Formate	ET-FORM	1.02e-12				32	1.02e-12	0%
Methyl Acetate	ME-ACET	3.49e-13	8.30e-13		0.517	32	2.65e-13	-24%
Methyl Propionate	ME-PRAT	1.03e-12				32	6.87e-13	-33%
n-Propyl Formate	C3-FORM	2.38e-12				32	2.37e-12	0%
Ethyl Acetate	ET-ACET	1.60e-12				3	1.72e-12	7%
Ethyl Propionate	ET-PRAT	2.14e-12				32	2.14e-12	0%
n-Butyl Formate	C4-FORM	3.12e-12				32	3.79e-12	21%
Methyl Butyrate	ME-BUAT	3.04e-12				32	1.91e-12	-37%



Table 8 (continued)

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
Propyl Acetate	PR-ACET	3.40e-12				3	3.21e-12	-6%
Isopropyl Acetate	IPR-ACET	3.40e-12				3	3.48e-12	2%
Methyl Isobutyrate	ME-IBUAT	1.73e-12				33	1.17e-12	-32%
t-Butyl Acetate	TBU-ACET	4.25e-13				34	5.56e-13	31%
s-Butyl Acetate	SBU-ACET	5.50e-12				3	5.34e-12	-3%
n-Propyl Propionate	PR-PRAT	4.02e-12				32	3.64e-12	-9%
Ethyl Butyrate	ET-BUAT	4.94e-12				32	3.36e-12	-32%
n-Butyl Acetate	BU-ACET	4.20e-12				3	4.63e-12	10%
n-Propyl Butyrate	PR-BUAT	7.41e-12				32	4.86e-12	-34%
n-Butyl Butyrate	BU-BUAT	1.06e-11				32	6.28e-12	-41%
Propylene Carbonate	PC	6.90e-13				36	3.79e-12	449%
Methyl Lactate	ME-LACT	2.76e-12				37	2.67e-12	-3%
Ethyl Lactate	ET-LACT	3.91e-12				37	4.12e-12	5%
Pr. Glycol Methyl Ether Acetate	PGME-ACT	1.44e-11				23	1.47e-11	2%
Dimethyl Succinate	DBE-4	1.50e-12				38	1.17e-12	-22%
Dimethyl Glutarate	DBE-5	3.50e-12				38	2.59e-12	-26%
Dimethyl Adipate	DBE-6	8.80e-12				38	4.01e-12	-54%
<u>Oxides</u>								
Ethylene Oxide	ETOX	7.60e-14				3	3.83e-13	404%
Propylene Oxide	PROX	5.20e-13				3	7.57e-13	46%
1,2-Epoxybutane	12BUOX	1.91e-12				39	2.00e-12	5%
<u>Acids</u>								
Formic Acid	FORMACID	4.50e-13	4.50e-13		0.000	3		
Acetic Acid	ACETACID	8.00e-13				14	2.10e-13	-74%
Propionic Acid	PROPACID	1.16e-12				14	1.34e-12	16%
<u>Aldehydes</u>								
Acetaldehyde	ACETALD	1.57e-11	5.60e-12		-0.616	15	1.58e-11	0%
Propionaldehyde	PROPALD	2.00e-11				15	2.01e-11	1%
2-Methylpropanal	2MEC3AL	2.60e-11	6.61e-12		-0.817	3	2.10e-11	-19%
Butanal	1C4RCHO	2.33e-11	5.26e-12		-0.886	3	2.14e-11	-8%
Pentanal	1C5RCHO	2.82e-11	6.34e-12		-0.890	3	2.28e-11	-19%
2,2-Dimethylpropanal (pivaldehyde)	22DMC3AL	2.63e-11	6.82e-12		-0.805	3	1.97e-11	-25%
3-Methylbutanal	3MC4RCHO	2.74e-11				3	2.28e-11	-17%
Acrolein	ACROLEIN	1.99e-11				3	3.16e-11	59%
Crotonaldehyde	CROTALD	3.64e-11				42	6.34e-11	74%
Methacrolein	METHACRO	3.33e-11	1.86e-11		-0.348	40	5.79e-11	74%
Hydroxy Methacrolein	HOMACR	4.30e-11				41	5.79e-11	35%
Isoprene Product #1	IP-MHY1	7.00e-11				41	8.71e-11	24%
Isoprene Product #2	IP-MHY2	7.00e-11				41	8.71e-11	24%
Isoprene Product #3	IP-HMY	7.00e-11				41	8.71e-11	24%

Table 8 (continued)

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	B	Ea kcal/mole	Ref	Est'd k(300) k (diff)
<u>Ketones</u>							
Acetone	ACETONE	2.22e-13	2.80e-12		1.510	15	2.09e-13 -6%
Cyclobutanone	CC4-KET	8.70e-13				18	4.42e-12 408%
Methyl Ethyl Ketone	MEK	1.20e-12	1.30e-12		0.050	17	1.35e-12 13%
Cyclopentanone	CC5-KET	2.94e-12				18	6.83e-12 132%
3-Pentanone	DEK	2.00e-12				3	2.49e-12 25%
2-Pentanone	MPK	4.56e-12				43	4.78e-12 5%
Cyclohexanone	CC6-KET	6.39e-12				18	1.21e-11 89%
Methyl t-Butyl Ketone	MTBK	1.21e-12				19	1.72e-12 42%
4-Methyl-2-Pentanone	MIBK	1.41e-11				3	8.82e-12 -37%
Methyl n-Butyl Ketone	MNBK	9.10e-12				3	6.77e-12 -26%
Di-Isopropyl Ketone	DIPK	5.38e-12				20	5.07e-12 -6%
2-Heptanone	C7-KET-2	1.17e-11				43	8.19e-12 -30%
2-Octanone	C8-KET-2	1.10e-11				19	9.61e-12 -13%
2-Nonanone	C9-KET-2	1.22e-11				19	1.10e-11 -10%
Di-isobutyl ketone (2,6-dimethyl-4-heptanone	DIBK	2.75e-11				3	1.74e-11 -37%
2-Decanone	C10-K-2	1.32e-11				19	1.24e-11 -6%
Methylvinyl ketone	MVK	1.87e-11	4.14e-12		-0.900	3	3.16e-11 69%
<u>Other Oxygenates</u>							
Hydroxy Acetone	HOACET	3.02e-12				16	3.11e-12 3%
Methoxy Acetone	MEOACET	6.77e-12				16	7.11e-12 5%
<u>Nitrogen-Containing Compounds</u>							
N-Methyl-2-Pyrrolidone	NMP	2.15e-11				36	
Toluene Diisocyanate	TDI	7.40e-12				45	
Ethyl Amine	ET-AMINE	2.76e-11	1.47e-11		-0.376	3	
Dimethyl Amine	DM-AMINE	6.58e-11	2.89e-11		-0.491	3	
Trimethyl Amine	TM-AMINE	6.07e-11	2.62e-11		-0.501	3	
Methyl Nitrite	ME-NITRT	2.20e-13				14	
<u>Halogen-Containing Compounds</u>							
Methyl Chloride	CH3-CL	4.48e-14	3.15e-13	2.0	1.163	14	
Dichloromethane	CL2-ME	1.45e-13	7.69e-13	2.0	0.994	3	
Methyl Bromide	ME-BR	4.12e-14	2.34e-13	2.0	1.035	3	
Chloroform	CHCL3	1.06e-13	5.67e-13	2.0	1.002	3	
Ethyl Chloride	S-043812	4.18e-13	6.94e-13	2.0	0.302	14	
Ethylene Dichloride	S-043815	2.53e-13	9.90e-13	2.0	0.813	14	
1,1-Dichloroethane	S-043813	2.60e-13				3	
1,1,2-Trichloroethane	S-043820	2.00e-13	4.00e-13	2.0	0.413	14	
1,1,1-Trichloroethane	111-TCE	1.24e-14	5.33e-13	2.0	2.244	3	
Ethyl Bromide	C2-BR	3.08e-13	2.72e-11		2.671	3	
Ethylene Dibromide	S-099014	2.27e-13	9.27e-13	2.0	0.839	14	

Table 8 (continued)

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	B	Ea kcal/mole	Ref	Est'd k(300) k (diff)
n-Propyl Bromide	C3-BR	1.18e-12				46	
n-Butyl Bromide	C4-BR	2.46e-12				46	
Vinyl Chloride	CL-ETHE	6.90e-12	1.69e-12		-0.839	14	
Trans-1,2-Dichloroethene	S-099018	2.32e-12	1.01e-12		-0.497	14	
Trichloroethylene	CL3-ETHE	2.34e-12	5.63e-13		-0.849	14	
Perchloroethylene	CL4-ETHE	1.71e-13	9.64e-12		2.403	14	
<u>Sulfur-Containing Compounds</u>							
Dimethyl Sulfide	DMS	4.85e-12	1.13e-11		0.505	14	
Dimethyl Sulfoxide	DMSO	6.20e-11				3	
<u>Silicon-Containing Compounds</u>							
Hexamethyldisiloxane	SI2OME6	1.38e-12				3	
Hydroxymethyldisiloxane'	SI2OMEOH	1.89e-12				3	
D4 Cyclosiloxane	(SIOME)4	1.00e-12				3	
D5 Cyclosiloxane	(SIOME)5	1.55e-12				3	

References

- 1 Rate constant expression recommended by Atkinson (1997a)
- 1a Atkinson et al, paper in preparation (1999)
- 1b Carter et al (1999d)
- 2 Room temperature rate constant from Carter et al (1999b).
- 3 Rate constant expression recommended by Atkinson (1989). Recommendation not changed in evaluation update by
- 4 Rate constant based on average of values for 1- and 2- isomers tabulated by Atkinson (1989).
- 5 Rate constant from Atkinson and Aschmann (1986).
- 6 Rate constant from Atkinson and Aschmann (1988a)
- 7 Rate constant from average of values for o-, m- and p- isomers tabulated by Atkinson (1989).
- 8 Rate constant based on data tabulated by Atkinson (1989) and consistent with more recent measurement given by Atkinson (1994).
- 9 Rate constant from Atkinson et al (1985).
- 10 Assumed to have same rate constant as n-propyl benzene
- 11 Rate constant from Atkinson and Aschmann (1987).
- 12 Rate constant from Baulch et al (1989).
- 13 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated based on data for similar alkenes.
- 14 Rate constant expression recommended by Atkinson (1994)
- 15 Rate expression recommended by IUPAC panel (Atkinson et al, 1997a).
- 16 Rate constant from Dagat et al (1988a).
- 17 Rate expression recommended by IUPAC panel (Atkinson et al, 1999).
- 18 Rate constant from Dagat et al (1988b).
- 19 Rate constant from Wallington and Kurylo (1987).
- 20 Rate constant from Atkinson et al (1982).
- 21 Rate constant used is Atkinson (1989) recommendation. k=8.1e-13 from Saunders et al (1994) not used because problems reported. k=1.43e-12 from Tuazon and co-workers (Carter et al, 1986c) does not fit chamber results (Carter et al, 1986c).

Table 8 (continued)

References (continued)

- 22 Rate constant from Wallington et al (1988a).
- 23 Rate constant from Carter et al (1999a).
- 24 Rate constant from Aschmann and Atkinson (1998).
- 25 Rate constant from Wallington et al (1990).
- 26 Rate constant from Bennett and Kerr (1989).
- 27 Rate constant from Wallington et al (1988b).
- 28 Rate constant of Dagaut et al (1988a) used. Value of Hartmann et al (1986) not consistent with chamber data (Carter
- 29 Average of values of Porter et al (1995) and Aschmann and Atkinson (1998)
- 30 Average of values of Dagaut et al (1988a), Stemmler et al (1996) and Aschmann and Atkinson (1998), as tabulated by Aschmann and Atkinson (1997).
- 31 Rate constant from Carter et al (1993a).
- 32 Rate constant from Wallington et al (1988d).
- 33 Rate constant from Wells et al. (1999).
- 34 Rate constant from Smith et al (1992). Average of values relative to propane and n-butane
- 35 Rate constant used is average of various measurements tabulated by Sidebottom et al (1997).
- 36 Rate constant from Carter et al (1996c).
- 37 Rate constant from Atkinson and Carter (1995).
- 38 Rate constant from Carter et al (1997e).
- 39 Rate constant from Wallington et al (1988c).
- 40 See Carter and Atkinson (1996) and references therein.
- 41 Rate constant estimated by Carter and Atkinson (1996).
- 42 Rate constant from Atkinson et al (1983).
- 43 Atkinson et al, paper in preparation (1999b)
- 44 Carter et al (unpublished results, 1999)
- 45 Becker et al (1988)
- 46 Donaghy et al. (1993)

## b. Estimation of OH Abstraction Rate Constants

Group rate constants for OH abstraction reactions are estimated using the group additivity method developed by Atkinson (1987), as updated by Kwok and Atkinson (1995), Kwok et al (1996) and in this work. The rate constant for the reaction of OH at any group is a function of the group and the groups bonded to it (the “neighbor groups”), and is derived from the equation

$$k(\text{OH} + \text{group}) = k(\text{group}) \prod_{\text{neighbor groups}} F(\text{neighbor group}) \quad (\text{I})$$

where “k(group)” is the rate constant for OH reaction at the group if it were only bonded to methyl radicals, and “F(neighbor group)” is the substituent correction factor for a neighbor group. The group rate constants and the currently implemented in the mechanism estimation system is given in Table 9. As indicated in the footnotes to the table, most of the group rate constants and correction factors were obtained from Kwok and Atkinson (1995), with one updated value from Kwok et al (1996) and with a few gaps filled in this work. Note that in some cases, the correction factor depends not only on the neighbor group but also the next nearest neighbor; these modified groups are referred to as “subgroups” on the table. Note also that formate -CHO groups are treated as separate groups as aldehyde -CHO for the

purpose of OH rate constant estimates. This is because OH abstraction reaction appears to be essentially negligible for the former, but very rapid for the latter.

If the compound has a C=C double bond anywhere in the molecule, at present the system assumes the abstraction reactions from any H-containing group are all negligible compared to the addition to the C=C double bond, and the abstraction rate constant is set at zero. Although methods exist for estimating these abstraction rate constants (Kwok and Atkinson, 1997), it is currently necessary to make this approximation because general methods for generating and estimating the rates of all the possible reactions of the unsaturated radicals formed in these reactions have not yet been developed. Ignoring these abstraction reactions from unsaturated compounds is not a bad approximation for smaller molecules such as propene and the butenes, and all known mechanisms currently used in atmospheric models incorporate this approximation. However, abstraction at groups away from the double bonds can become non-negligible for the larger alkenes (see Atkinson, 1997a and references therein), so this approximation should be removed once methods to generate and estimate reactions of unsaturated radicals are developed.

Table 9. Group rate constants and substituent factors used to estimate OH radical abstraction rate constants.

Group	$k(\text{group}) = A T^B e^{-D/T}$ ( $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ )					F(group)		F(subgroup)		
	k(298)	A	B	D	Ref	F	Ref	Subgroup	F	Ref
-CH <sub>3</sub>	1.36e-13	4.49e-18	2	320	a	1.00	a			
-CH <sub>2</sub> -	9.34e-13	4.50e-18	2	-253	a	1.23	a	-CH <sub>2</sub> (CO-)	3.90	a
								-CH <sub>2</sub> (CO-O-)	1.23	a
								-CH <sub>2</sub> (F)	0.61	a
								-CH <sub>2</sub> (Cl)	0.36	a
								-CH <sub>2</sub> (Br)	0.46	a
>CH-	1.95e-12	2.12e-18	2	-696	a	1.23	a	-CH(CO-)-	3.90	a
								-CH(CO-O-)-	1.23	a
								-CH(F)-	0.21	a
								-CH(Cl)-	0.36	a
								-CH(Br)-	0.46	a
>C<						1.23		>C(CO-)-	3.90	a
								>C(CO-O-)-	1.23	a
								>C(F)-	0.21	a
								>C(Cl)-	0.36	a
								>C(Br)-	0.46	a
-O-						8.40	a	-O(CO-)	1.60	a
								-O(CHO)-	0.90	e
								-O(NO <sub>2</sub> )-	0.04	a
-OH	1.40e-13	2.10e-18	2	85	a	3.50	a			
-CHO	1.58e-11	5.55e-12	0	-311	b	0.75	a			
HCO(O)-	0.00e+00				c	-				
-CO-						0.75	a	-CO(O-)	0.31	d
-ONO <sub>2</sub>						0.04	a			
-F						0.09	a			
-Cl						0.38	a			
-Br						0.28	a			
-I						0.53	a			
-NO <sub>2</sub>						0.00	a			

References

- a Kwok and Atkinson (1995)
- b Based on kOH for acetaldehyde (Atkinson et al, 1997a, 1999)
- c Reaction at formate group assumed to be negligible based on low OH + formate rate constants (Atkinson, 1989)
- d Updated value from Kwok et al (1996)
- e Adjusted to fit experimental kOH's for ethyl and methyl formate. (Does not work well for methyl formate, but assigned kOH is used for that compound.)

### c. Estimation of OH Addition Rate Constants

Rate constant estimates for additions to double bonds are made by estimating total rate constants for reaction at a double bond with a given number and configuration of substituents, and then, for unsymmetrical molecules, estimating the fraction that reacts at the each end. These estimates are shown on Table 10, along with an indication of the derivation of the values used. The total rate constant estimates are based on measured rate constants for representative molecules, but only limited information is available upon which to base the branching ratio estimates,

These estimates are then used to derive a group rate constant for each of the two groups around the double bond. Note that since the present system does not support generating mechanisms with more than one C=C double bond (except for “special reactants”, as discussed later), the estimates on this table are only applicable to monoalkenes.

The group rate constant estimates on Table 10 are somewhat different than those given by Kwok and Atkinson (1997) for several reasons. Propene is not used when deriving the group rate constants for monosubstituted alkenes because its OH rate constant is known and kinetic data for the higher 1-alkenes, which are expected to be more similar to the types of compounds for which estimates may be needed, are better fit by slightly higher values. The estimates of Kwok and Atkinson (1997) also take into account the possibility that some of the reaction may be occurring by abstraction from other groups, which is ignored in our estimates (see below). Kwok and Atkinson (1997) give correction factors for oxygenated substituents, but these are also not fully implemented in the present system because in this work estimates are mainly needed only for hydrocarbon species. The few unsaturated oxygenated species that are handled by the system (primarily acrolein and isoprene products) already have measured or assigned total OH rate constants (e.g., see Carter and Atkinson, 1996). However, correction factors from Kwok and Atkinson (1997) for -CHO and -CO- substituents, of 0.35 and 0.9, respectively, have been incorporated on a preliminary basis.

Table 10. Group rate constants used for estimating rates of OH addition reactions.

Group	Estimated Total Rate Constant (300K) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	Fraction reacting at least substituted end
CH <sub>2</sub> =CH-	3.16e-11 Total rate constant based on average for 300K rate constants for 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene and 3-3-dimethyl-1-butene (Atkinson, 1997a).	0.65 Terminal bond addition fraction from Cvetanovic (1976).
CH <sub>2</sub> =C<	5.79e-11 Total rate constant based on average for 300K rate constants for isobutene, 2-methyl-1-butene and 2-methyl-1-pentene (Atkinson, 1997a).	1.00 100% addition at terminal end assumed.
-CH=CH-	6.33e-11 Total rate constant based on average for 300K rate constants for the 2-butenes, the 2-pentenenes, trans-4-methyl-2-pentene, trans-4,4-dimethyl-2-pentene, trans-2-heptene, trans-4-octene, cyclopentene, and cyclohexene (Atkinson, 1997a).	0.50 Equal addition at each position assumed.
-CH=C<	8.70e-11 Total rate constant based on average for 300K rate constants for 2-methyl-2-butene and 2-methyl-2-pentene (Atkinson, 1997a).	0.75 No information available concerning relative addition rates at the different positions. Roughly estimate 75% addition at the least substituted position.
>C=C<	1.05e-10 Total rate constant based on average for 300K rate constants for 2,3-dimethyl-2-butene and 2,3-dimethyl-2-pentene (Atkinson, 1997a).	0.50 Equal addition at each position assumed.



#### d. Comparison of Estimated and Assigned Rate Constants

Table 8, above, shows a comparison of the estimated and assigned OH radical rate constants, from which one can obtain an indication of the overall performance of the estimation methods for the various types of VOCs. Table 11 shows a summary of average percentage errors (biases) and average absolute percentage errors (errors) for OH radical rate constant estimates for various classes of VOCs. It can be seen that the estimation method performs reasonably well for alkanes and alkenes, having essentially no bias and an average error of less than 15%. The estimates do not perform as well for the oxygenated compounds, and appears to be biased high in the case of aldehydes and ketones. Refinements to the estimation method may improve the performance for these oxygenates, but updating the work of Kwok and Atkinson (1995) was beyond the scope of this report.

Table 11. Summary of average biases and errors in estimates of OH radical rate constants from data given on Table 8.

Class	Count	Average	
		Bias	Error
Alkanes	43	1%	10%
Alkenes	25	1%	7%
Alcohols and Glycols	41	-11%	22%
Esters	26	5%	36%
Aldehydes	14	16%	29%
Ketones	34	36%	56%
Others	2	4%	4%

Notes:

Bias is average of percentage differences between experimental and estimated values

Error is average of absolute value of percentage differences.

#### e. Assigned Mechanisms for Initial OH Reactions

Because estimation methods for the branching ratios for the reactions of OH radicals at different positions of the molecule have some uncertainty, branching ratios are explicitly assigned for those compounds where experimental data are available, and indicate that the estimates may not be appropriate. In addition, as indicated in Table 7, several alkynes and dialkenes have also been incorporated into the mechanism generation system as “special reactants”, whose reactions cannot be estimated and therefore need to be specified explicitly. The explicitly assigned branching ratios for initial OH radical reactions that are currently incorporated in the system are summarized on Table 12, along with the basis for the various assignments that are used.

Table 12. Assigned mechanisms for the initial reactions of OH radicals with compounds for which estimates could not be made, or where experimental data indicate that the estimates may not be appropriate.

Reactant and Products [a]	Factor	Documentation
<u>1,3-Butadiene</u> [CH <sub>2</sub> =CH-CH=CH <sub>2</sub> ] CH <sub>2</sub> =CH-CH[.] -CH <sub>2</sub> -OH	100.0%	Terminal addition assumed to dominate because of formation of resonance-stabilized radical.
<u>Isoprene</u> [CH <sub>2</sub> =CH-C(CH <sub>3</sub> )=CH <sub>2</sub> ] CH <sub>2</sub> =CH-C[.](CH <sub>3</sub> )-CH <sub>2</sub> -OH	52.4%	Mechanism assumed to be as discussed by Carter and Atkinson (1996).
CH <sub>2</sub> =C(CH <sub>3</sub> )-CH[.] -CH <sub>2</sub> -OH	42.6%	See above.
CH <sub>2</sub> =CH-C(OH)(CH <sub>2</sub> .)-CH <sub>3</sub>	2.5%	Based on observed 3-methyl furan yields as discussed by Carter and Atkinson (1996).
CH <sub>2</sub> =C(CH <sub>3</sub> )-CH(CH <sub>2</sub> .)-OH	2.5%	See above.
<u>Acetylene</u> [HC::CH] HO-CH=CH.	90.0%	Estimated mechanism is based on the data of Hatakeyama et al (1986) and modeling acetylene environmental chamber runs Carter et al (1997c).
HCO-CH <sub>2</sub> .	10.0%	See above. Adjusted to fit chamber data.
<u>Methyl Acetylene</u> [HC::C-CH <sub>3</sub> ] CH <sub>3</sub> -C[.] =CH-OH	100.0%	Estimated to be the major reaction pathway.
<u>Ethyl Acetylene</u> [HC::C-CH <sub>2</sub> -CH <sub>3</sub> ] CH <sub>3</sub> -CH <sub>2</sub> -C[.] =CH-OH	100.0%	Estimated to be the major reaction pathway.
<u>2-Butyne</u> [CH <sub>3</sub> -C::C-CH <sub>3</sub> ] CH <sub>3</sub> -C(OH)=C[.] -CH <sub>3</sub>	100.0%	Estimated to be the major reaction pathway.
<u>Methanol</u> [CH <sub>3</sub> -OH] HO-CH <sub>2</sub> .	85.0%	Branching ratios recommended by IUPAC (Atkinson et al, 1997a, 1999).
CH <sub>3</sub> O.	15.0%	See above.
<u>Ethanol</u> [CH <sub>3</sub> -CH <sub>2</sub> -OH] CH <sub>3</sub> -CH[.] -OH	90.0%	Branching ratios recommended by IUPAC (Atkinson et al, 1997a, 1999).
CH <sub>3</sub> -CH <sub>2</sub> O.	5.0%	See above
HO-CH <sub>2</sub> -CH <sub>2</sub> .	5.0%	See Above
<u>1-Octanol</u> [CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH] CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -OH	19.2%	Based on yields of octanal from 1-octanol (Carter et al, 1999a).
HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	1.5%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH <sub>3</sub> -CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	10.8%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	13.3%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	13.3%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	13.3%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -OH	13.3%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -OH	13.3%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> O.	1.7%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
<u>2-Octanol [CH<sub>3</sub>-CH(OH)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -C[.](OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	36.5%	Based on yield of 2-octanone from 2-octanol (Carter et al, 1999a)
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(CH <sub>2</sub> .)-OH	1.5%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>3</sub>	1.5%	See above.
CH <sub>3</sub> -CH(OH)-CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	12.3%	See above.
CH <sub>3</sub> -CH(OH)-CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	12.3%	See above.
CH <sub>3</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -CH <sub>3</sub>	12.3%	See above.
CH <sub>3</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>3</sub>	12.3%	See above.
CH <sub>3</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>3</sub>	9.9%	See above.
CH <sub>3</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	1.5%	See above.
<u>3-Octanol [CH<sub>3</sub>-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -CH <sub>2</sub> -C[.](OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	42.4%	Based on yield of 3-octanone from 3-octanol (Carter et al, 1999a)
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> .	1.4%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH[.] -CH <sub>3</sub>	9.4%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>2</sub> -CH <sub>3</sub>	1.4%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH(OH)-CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	11.5%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -CH <sub>3</sub>	11.5%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>3</sub>	11.5%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>3</sub>	9.4%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	1.4%	See above.
<u>4-Octanol [CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C[.](OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	36.6%	Based on yield of 4-octanone from 4-octanol (Carter et al, 1999a)
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	1.6%	Relative branching ratios of other routes estimated using method of Kwok and Atkinson (1995).
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH[.] -CH <sub>3</sub>	10.3%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH[.] -CH <sub>2</sub> -CH <sub>3</sub>	12.7%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	1.6%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH[.] -CH <sub>2</sub> -CH <sub>3</sub>	12.7%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH[.] -CH <sub>3</sub>	12.7%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -CH <sub>3</sub>	10.3%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	1.6%	See above.
<u>Methyl t-Butyl Ether [CH<sub>3</sub>-C(CH<sub>3</sub>)(CH<sub>3</sub>)-O-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH <sub>2</sub> .	80.0%	Branching ratios based on product studies of Tuazon et al, (1991b); and Smith et al (1991), with overall yields increased to account for 100% reaction.
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> .)-O-CH <sub>3</sub>	20.0%	See Above

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
<u>1-Methoxy-2-Propanol [CH<sub>3</sub>-CH(OH)-CH<sub>2</sub>-O-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -O-CH <sub>2</sub> -CH(CH <sub>2</sub> .)-OH	0.0%	Estimated to be minor
CH <sub>3</sub> -C[.](OH)-CH <sub>2</sub> -O-CH <sub>3</sub>	39.0%	Based on observed methoxyacetone yields (Tuazon et al, 1998a).
CH <sub>3</sub> -O-CH <sub>2</sub> -CH[O.] -CH <sub>3</sub>	0.0%	Estimated to be minor
CH <sub>3</sub> -CH(OH)-CH[.] -O-CH <sub>3</sub>	58.0%	Based on observed methyl formate and acetaldehyde yields, the expected products from this route (Tuazon et al, 1998a)
CH <sub>3</sub> -CH(OH)-CH <sub>2</sub> -O-CH <sub>2</sub> .	3.0%	Estimated to occur ~6% of the time. 3% yield assumed to account for 100% reaction.
<u>2-Butoxy-Ethanol [CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-OH]</u>		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[.] -CH <sub>2</sub> -OH	57.0%	Branching ratio based on observed yield of n-butyl formate, which is the expected major product from this route (Tuazon et al, 1998a).
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[.] -O-CH <sub>2</sub> -CH <sub>2</sub> -OH	22.0%	Branching ratio based on observed yields of 2-hydroxyethyl formate and propanal, the expected major products from this route (Tuazon et al, 1998a).
HO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	0.5%	Relative branching ratios for this and the other routes estimated using method of Kwok and Atkinson (1996).
CH <sub>3</sub> -CH[.] -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -OH	3.5%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -OH	4.3%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH[.] -OH	12.2%	See above.
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> O.	0.6%	See above.
<u>Methyl Acetate [CH<sub>3</sub>-O-CO-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -CO-O-CH <sub>2</sub> .	100.0%	Environmental chamber reactivity data fit somewhat better if reaction at the CH <sub>3</sub> -CO end is assumed to be negligible.
CH <sub>3</sub> -O-CO-CH <sub>2</sub> .	0.0%	See above
<u>Propylene Carbonate [*CH(CH<sub>3</sub>)-CH<sub>2</sub>-O-CO-O-*]</u>		
*CH(CH <sub>2</sub> .)-CH <sub>2</sub> -O-CO-O-*	25.0%	Branching ratio estimated from ratio of estimate for reaction at this position using method of Kwok and Atkinson (1996) to measured total rate constant Carter et al, 1996c).
*C[.](CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-O-*	37.5%	Model simulations are somewhat more consistent with environmental chamber reactivity data if the other two reaction routes are assumed to occur with approximately equal probability.
*CH(CH <sub>3</sub> )-O-CO-O-CH[.] -*	37.5%	See above
<u>Methyl Isobutyrate [CH<sub>3</sub>-CH(CH<sub>3</sub>)-CO-O-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -C[.](CH <sub>3</sub> )-CO-O-CH <sub>3</sub>	67.0%	Branching ratio derived from total rate constant and estimated rate constants for the competing reaction routes. This results in higher predicted yields for acetone, which is more consistent with the product data of Wells et al (1999).
CH <sub>3</sub> -CH(CH <sub>2</sub> .)-CO-O-CH <sub>3</sub>	20.0%	Branching ratio derived from ratio of rate constant for this route estimated using the method of Kwok and Atkinson (1995), relative to the total rate constant.
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CO-O-CH <sub>2</sub> .	13.0%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
<u>Propylene Glycol Methyl Ether Acetate [CH<sub>3</sub>-O-CH(CH<sub>3</sub>)-CH<sub>2</sub>-O-CO-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> .	7.9%	Group rate constant estimated using method of Kwok and Atkinson (1995)
CH <sub>3</sub> -O-C[.](CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-CH <sub>3</sub>	45.3%	Group rate constant adjusted to fit environmental chamber reactivity data, and to be consistent with measured total rate constant.
CH <sub>3</sub> -O-CH(CH <sub>2</sub> .)-CH <sub>2</sub> -O-CO-CH <sub>3</sub>	1.2%	Group rate constant estimated using method of Kwok and Atkinson (1995)
CH <sub>3</sub> -O-CH(CH <sub>3</sub> )-CH[.]-O-CO-CH <sub>3</sub>	45.3%	Group rate constant adjusted to fit environmental chamber reactivity data, and to be consistent with measured total rate constant.
CH <sub>3</sub> -O-CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-CH <sub>2</sub> .	0.3%	Group rate constant estimated using method of Kwok and Atkinson (1995)
<u>Dimethyl Adipate (DBE-5) [CH<sub>3</sub>-O-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-O-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO-O-CH <sub>2</sub> .	39.0%	Based on yield of CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO-OH observed by Tuazon et al (1999)
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH[.]-CH <sub>2</sub> -CO-O-CH <sub>3</sub>	41.0%	Yield of CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CO-CH <sub>2</sub> -CO-O-CH <sub>3</sub> observed by Tuazon et al (1999) corresponds to this route occurring 33% of the time. However, model simulations fit chamber data somewhat better if this route is assumed to be relatively more important; so the fraction reacted at in this position is estimated from the ratio of the rate constant derived using estimates of Kwok and Atkinson (1985) as updated by Kwok et al (1996) to the measured total rate constant. This is within the uncertainty of the yield measurement.
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CH[.]-CO-O-CH <sub>3</sub>	20.0%	See above
<u>Acrolein [CH<sub>2</sub>=CH-CHO]</u>		
CH <sub>2</sub> =CH-CO.	75.0%	Estimated rate constant for reaction at this position is intermediate between the estimate based on the analogous reaction of methacrolein and estimation using method of Atkinson (1987).
HCO-CH[.]-CH <sub>2</sub> -OH	17.0%	Addition to double bond assumed to occur 25% of the time, based on total rate constant and estimate for reaction at the CHO position. Terminal/internal ratio based on the ratio determined for OH + propene.
HCO-CH(CH <sub>2</sub> .)-OH	8.0%	See above.
<u>Crotonaldehyde [CH<sub>3</sub>-CH=CH(CHO)]</u>		
CH <sub>3</sub> -CH=CH(CO.)	45.0%	Assumed to occur with the same rate constant as the analogous reaction for methacrolein.
CH <sub>3</sub> -CH[.]-CH(OH)-CHO	27.5%	Fraction reacted based on total rate constant, estimated rate for abstraction from -CHO, and assumption that addition at each side of the double bond is equal.
CH <sub>3</sub> -CH(OH)-CH[.]-CHO	27.5%	See above.

Table 12 (continued)

Reactant and Products [a]	Factor	Documentation
<u>Methacrolein [CH<sub>2</sub>=C(CHO)-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -C[.](CHO)-CH <sub>2</sub> -OH	44.0%	Adjusted to give same product distribution as used by Carter and Atkinson (1996), and to be consistent with available product data.
CH <sub>3</sub> -C(OH)(CH <sub>2</sub> .)-CHO	6.0%	See above.
CH <sub>2</sub> =C(CO.)-CH <sub>3</sub>	50.0%	See above.
<u>Hydroxy Methacrolein [CH<sub>2</sub>=C(CHO)-CH<sub>2</sub>-OH]</u>		
CH <sub>2</sub> =C(CO.)-CH <sub>2</sub> -OH	38.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HO-CH <sub>2</sub> -C[.](CHO)-CH <sub>2</sub> -OH	52.0%	See above.
HCO-C(OH)(CH <sub>2</sub> .)-CH <sub>2</sub> -OH	10.0%	See above.
<u>Isoprene Product #1 [CH<sub>3</sub>-C(CHO)=CH(CH<sub>2</sub>-OH)]</u>		
CH <sub>3</sub> -C(CO.)=CH(CH <sub>2</sub> -OH)	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH <sub>3</sub> -C[.](CHO)-CH(OH)-CH <sub>2</sub> -OH	50.0%	See above.
CH <sub>3</sub> -C(CHO)(OH)-CH[.]-CH <sub>2</sub> -OH	25.0%	See above.
<u>Isoprene Product #2 [CH<sub>3</sub>-C(CHO)=CH-CH<sub>2</sub>-OH]</u>		
CH <sub>3</sub> -C(CO.)=CH-CH <sub>2</sub> -OH	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH <sub>3</sub> -C[.](CHO)-CH(OH)-CH <sub>2</sub> -OH	50.0%	See above.
CH <sub>3</sub> -C(CHO)(OH)-CH[.]-CH <sub>2</sub> -OH	25.0%	See above.
<u>Isoprene Product #3 [HCO-CH=C(CH<sub>3</sub>)-CH<sub>2</sub>-OH]</u>		
HO-CH <sub>2</sub> -C(CH <sub>3</sub> )=CH-CO.	25.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH(OH)-C[.](CH <sub>3</sub> )-CH <sub>2</sub> -OH	50.0%	See above.
HCO-CH[.]-C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -OH	25.0%	See above.
<u>Cyclohexanone [*CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-*]</u>		
*CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO-CH[.]-*	44.0%	Better fits of model simulations to results of environmental chamber reactivity experiments are obtained if equal probability of reaction at alpha and beta positions (Carter et al, 1999a).
*CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO-CH <sub>2</sub> -CH[.]-*	44.0%	See above.
*CH <sub>2</sub> -CH <sub>2</sub> -CO-CH <sub>2</sub> -CH <sub>2</sub> -CH[.]-*	12.0%	Approximately the fraction reacted at this position estimated by method of Kwok and Atkinson (1995)
<u>Methylvinyl ketone [CH<sub>2</sub>=CH-CO-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -CO-CH[.]-CH <sub>2</sub> -OH	70.0%	Based on product distribution of Tuazon and Atkinson (1989), as discussed by Carter and Atkinson (1996)
CH <sub>3</sub> -CO-CH(CH <sub>2</sub> .)-OH	30.0%	See above.
<u>Formic Acid [HCO-OH]</u>		
HCO <sub>2</sub> .	100.0%	Believed to be the major reaction route.

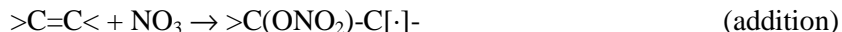
[a] Formation of H<sub>2</sub>O, when applicable, is not shown.

#### 4. Reactions with NO<sub>3</sub> Radicals

Reactions with NO<sub>3</sub> radicals can be a non-negligible fate for alkenes and aldehydes under some conditions, and therefore are included in the mechanism. These reactions are considered in essentially the same way as reaction with OH radicals, except that HNO<sub>3</sub> or ONO<sub>2</sub>-substituted products are formed. Thus, if the group has an abstractable hydrogen, the reaction is



And if it has a double bond, the reaction is



However, the current system assumes that rate constants for all abstraction reactions are negligible except for reaction at aldehyde -CHO groups. Therefore, only H abstraction reactions of NO<sub>3</sub> with aldehydes or additions to alkenes are considered in the current mechanism.

##### a. Assigned NO<sub>3</sub> Radical Rate Constants

NO<sub>3</sub> radical rate constants have been measured for a number of VOCs in the current mechanism, though the coverage is nowhere near as complete as is the case for the OH radical reaction. Table 13 gives the NO<sub>3</sub> radical rate constants assigned to all VOCs in the current mechanism for which the reaction with NO<sub>3</sub> radicals is represented. Note that the table does not include measured NO<sub>3</sub> radical rate constants for alkanes and other species that the current mechanism neglects as being of negligible importance. Footnotes indicate the basis for the rate parameter assignments, most of which are based on Atkinson (1991, 1994, 1997a) recommendations.

Table 13. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with NO<sub>3</sub> radicals in the present mechanism.

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	B	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
Propene	PROPENE	9.73e-15	4.59e-13		2.297	1	1.38e-14	42%
1-Butene	1-BUTENE	1.38e-14	3.14e-13		1.864	1	1.38e-14	0%
Isobutene	ISOBUTEN	3.32e-13	3.32e-13		0.000	2	3.32e-13	0%
cis-2-Butene	C-2-BUTE	3.47e-13	1.10e-13		-0.687	3	3.70e-13	7%
trans-2-Butene	T-2-BUTE	3.92e-13	1.10e-13	2.0	-0.759	1	3.70e-13	-6%
2-Methyl-2-Butene	2M-2-BUT	9.37e-12	9.37e-12		0.000	2	9.37e-12	0%
2,3-Dimethyl-2-Butene	23M2-BUT	5.72e-11	5.72e-11		0.000	2	5.72e-11	0%
Cyclopentene	CYC-PNTE	5.30e-13	5.30e-13		0.000	2	3.70e-13	-30%
Cyclohexene	CYC-HEXE	5.88e-13	1.05e-12		0.346	1	3.70e-13	-37%
1,3-Butadiene	13-BUTDE	1.00e-13	1.00e-13		0.000	2		
Isoprene	ISOPRENE	6.85e-13	3.03e-12		0.886	1		
a-Pinene	A-PINENE	6.09e-12	1.19e-12		-0.974	1		
3-Carene	3-CARENE	9.10e-12	9.10e-12		0.000	2		
b-Pinene	B-PINENE	2.51e-12	2.51e-12		0.000	2		
Sabinene	SABINENE	1.00e-11	1.00e-11		0.000	2		
d-Limonene	D-LIMONE	1.22e-11	1.22e-11		0.000	2		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	1.00e-15				4		
Styrene	STYRENE	1.51e-13				5		
Acetaldehyde	ACETALD	2.84e-15	1.40e-12		3.696	6		
Methylvinyl ketone	MVK	0.00e+00				7		
Methacrolein	METHACRO	4.76e-15	1.50e-12		3.430	8		
Isoprene Product #1	IP-MHY1	1.00e-13				9		
Isoprene Product #2	IP-MHY2	1.00e-13				9		
Isoprene Product #3	IP-HMY	1.00e-13				9		
Hydroxy Methacrolein	HOMACR	4.76e-15	1.50e-12		3.430	10		
Crotonaldehyde	CROTALD	5.12e-15				11		
N-Methyl-2-Pyrrolidone	NMP	1.26e-13				12		

#### References

- 1 Rate constant expression recommended by Atkinson (1997a)
- 2 Rate constant from Atkinson (1997a). Temperature dependence is assumed to be small.
- 3 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for trans-2-butene.
- 4 This rate constant estimated by Atkinson (private communication, 1997) based on the rate constant for NO<sub>3</sub> + Allyl chloride (Atkinson, 1991)
- 5 Rate constant from Atkinson and Aschmann (1988a).
- 6 Rate constant expression recommended by IUPAC, Supplement V (Atkinson et al, 1997a).
- 7 Data of Kwok et al (1997) indicate that the total rate constant is less than 6e-18 cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, which make it unimportant under atmospheric conditions.
- 8 Total rate constant from Kwok et al (1996). Temperature dependence estimated by Carter and Atkinson (1996)
- 9 Rate constant estimated by Carter and Atkinson (1996).
- 10 Rate constant assumed to be the same as for methacrolein (Carter and Atkinson, 1996)
- 11 Atkinson et al (1987)
- 12 Rate constant from Carter et al (1996c).



## b. Estimated NO<sub>3</sub> Radical Rate Constants

Reaction of NO<sub>3</sub> with aldehyde groups are based on the measured rate constant for the reaction of NO<sub>3</sub> with acetaldehyde, which is (Atkinson et al, 1997a, 1999),

$$k(\text{NO}_3 + \text{X-CHO}) = 1.40 \times 10^{-12} e^{-3.696/RT} \cdot F(\text{X}) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

where F(X) is the substituent factor for groups other than -CH<sub>3</sub> bonded to the -CHO. The correlation between NO<sub>3</sub> and OH radical abstraction rate constants given by Atkinson (1991)<sup>5</sup> is used to estimate these group substituent correction factors, F(X), which are as follows:

- F(-CH<sub>2</sub>-) = F(-CH-) = F(>C<) = 1.34 is derived from the correlation of Atkinson (1991) and the rate constant for OH abstraction from -CHO groups derived by the group-additivity method of Kwok and Atkinson (1995).
- F(-CHO) = 0.18 is derived from the correlation and the OH rate constant for glyoxal.
- F(-CO-) = 0.89 is derived from the correlation and the OH rate constant for methyl glyoxal.

Note that rate constants for NO<sub>3</sub> abstraction from -CHO groups an oxygen (e.g., formates and acids) are estimated to be zero, so such reactions are not generated.

The group rate constants used for estimating NO<sub>3</sub> addition rate constants is given on Table 14, along with the documentation for the rate constant assignments. Note that in the case of NO<sub>3</sub> reactions we assume that addition always occurs to the least substituted position around the bond, based on the assumption that since NO<sub>3</sub> addition rate constants are lower than those for OH addition, they will tend to be more selective. Rate constant data are available for only a few compounds of each type, so the estimates are necessarily more uncertain than those for OH radical reactions. As with the OH addition estimates, the rate constant for propene is not used for making the estimates for general 1-alkenes because 1-butene is considered to be more representative of the types of the higher monoalkenes for which rate constant estimates would be needed.

The group rate constants shown on Table 14 are strictly speaking applicable only for estimating rate constants for unsaturated hydrocarbons. Group correction factors, which are multiplied by the group rate constants shown on Table 14, are used for estimating rate constants for NO<sub>3</sub> to double bonds in unsaturated carbonyls. These are as follows:

- A factor of 0.007 is used if the double bond has a -CHO substituent, based on the ratio of the estimated rate constant for NO<sub>3</sub> addition to methacrolein (Carter and Atkinson, 1996) to the group rate constant for CH<sub>2</sub>=C<.
- A factor of  $2 \times 10^{-4}$  is used if the double bond has a -CO- substituent, based on the upper limit rate constant for the reaction of NO<sub>3</sub> with methyl vinyl ketone (Carter and Atkinson, 1996). The actual upper limit rate constant of  $6 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  corresponds to a factor of  $\sim 4 \times 10^{-4}$ , but we arbitrarily use a factor which is half that. This is sufficiently small to make reactions of NO<sub>3</sub> with such compounds to be of negligible importance.

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<sup>5</sup> Atkinson (1993) noted a good correlation between OH and NO<sub>3</sub> abstraction rate constants per abstractable hydrogen, with the data being fit by  $\ln k_{\text{NO}_3} = 6.498 + 1.611 \ln k_{\text{OH}}$ .

Table 14. Group rate constants and group substituent correction factors used for estimating rates of NO<sub>3</sub> addition reactions.

Groups	Estimated Total Rate Constant (300K) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	Fraction reacting at least substituted end
CH <sub>2</sub> =CH-	1.38e-14 Total rate constant based on 300K value for 1-butene (Atkinson, 1997a).	1.0 100% addition at terminal end assumed.
CH <sub>2</sub> =C<	3.32e-13 Total rate constant based on 300K value for isobutene (Atkinson, 1997a)	1.0 100% addition at terminal end assumed.
-CH=CH-	1.85e-13 Total rate constant based on averaging the 300K values for cis and trans 2-butene (Atkinson, 1997a).	0.5 Equal addition at each position assumed.
-CH=C<	9.37e-12 Total rate constant based on 300K value for 2-methyl-2-butene (Atkinson, 1997a).	1.0 100% Addition at the least substituted end is assumed.
>C=C<	2.86e-11 Total rate constant based on the 300K value for 2,3-dimethyl-2-butene (Atkinson, 1997a).	0.5 Equal addition at each position assumed.

The performance of the estimation method in predicting the measured NO<sub>3</sub> radical rate constants is indicated on Table 13. Except for propene (for which estimates are not needed) and the halogenated alkene on the list (whose subsequent reactions are not currently supported by the system), the estimates generally perform reasonably well. Of course, in most cases this is because the estimates are based on these data. There does seem to be a bias towards underpredicting the rate constants for the cycloalkenes, and it may be appropriate to add a ring correction term for such compounds.

### c. Assigned Mechanisms for Initial NO<sub>3</sub> Reactions

As with OH reactions discussed above, explicit assignments are used for the initial reactions for those VOCs where estimates cannot be made, where available experimental data indicate the estimates are inappropriate, or where alternative estimates are used. The explicitly assigned branching ratios for the initial NO<sub>3</sub> radical reactions that are currently incorporated in the system are summarized on Table 15, along with the basis for the various assignments that are used.

Table 15. Assigned mechanisms for the reactions of NO<sub>3</sub> radicals with compounds for which estimates could not be made, or where experimental data or other considerations indicate that the general estimates may not be appropriate.

Reactant and Products	Factor	Documentation
<u>1,3-Butadiene</u> [CH <sub>2</sub> =CH-CH=CH <sub>2</sub> ] CH <sub>2</sub> =CH-CH[.] -CH <sub>2</sub> -ONO <sub>2</sub>	100.0%	Terminal addition assumed to dominate because of formation of resonance-stabilized radical.
<u>Isoprene</u> [CH <sub>2</sub> =CH-C(CH <sub>3</sub> )=CH <sub>2</sub> ] CH <sub>2</sub> =CH-C[.](CH <sub>3</sub> )-CH <sub>2</sub> -ONO <sub>2</sub>	100.0%	Mechanism of Carter and Atkinson (1996) is assumed.
<u>Crotonaldehyde</u> [CH <sub>3</sub> -CH=CH(CHO)] CH <sub>3</sub> -CH=CH(CO.)	45.0%	Assumed to occur with the same rate constant as the analogous reaction for methacrolein.
CH <sub>3</sub> -CH[.] -CH(ONO <sub>2</sub> )-CHO	27.5%	Fraction reacted based on total rate constant, estimated rate for abstraction from -CHO, and assumption that addition at each side of the double bond is equal.
CH <sub>3</sub> -CH(ONO <sub>2</sub> )-CH[.] -CHO	27.5%	See above.
<u>Methacrolein</u> [CH <sub>2</sub> =C(CHO)-CH <sub>3</sub> ] HNO <sub>3</sub> + CH <sub>2</sub> =C(CO.)-CH <sub>3</sub> CH <sub>3</sub> -C[.](CHO)-CH <sub>2</sub> -ONO <sub>2</sub>	50.0% 50.0%	Mechanism of Carter and Atkinson (1996) is assumed. See above.
<u>Hydroxy Methacrolein</u> [CH <sub>2</sub> =C(CHO)-CH <sub>2</sub> -OH] HNO <sub>3</sub> + CH <sub>2</sub> =C(CO.)-CH <sub>2</sub> -OH HO-CH <sub>2</sub> -C[.](CHO)-CH <sub>2</sub> -ONO <sub>2</sub>	50.0% 50.0%	Mechanism of Carter and Atkinson (1996) is assumed. See above.
<u>Isoprene Product #1</u> [CH <sub>3</sub> -C(CHO)=CH(CH <sub>2</sub> -OH)] CH <sub>3</sub> -C[.](CHO)-CH(ONO <sub>2</sub> )-CH <sub>2</sub> -OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.
<u>Isoprene Product #2</u> [CH <sub>3</sub> -C(CHO)=CH-CH <sub>2</sub> -OH] CH <sub>3</sub> -C[.](CHO)-CH(ONO <sub>2</sub> )-CH <sub>2</sub> -OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.
<u>Isoprene Product #3</u> [HCO-CH=C(CH <sub>3</sub> )-CH <sub>2</sub> -OH] HCO-CH(ONO <sub>2</sub> )-C[.](CH <sub>3</sub> )-CH <sub>2</sub> -OH	100.0%	Mechanism of Carter and Atkinson (1996) is assumed. Abstraction from -CHO is estimated to occur only ~4% of the time.

## 5. Reactions with O<sub>3</sub>

Reactions with O<sub>3</sub> are assumed to occur only at carbon-carbon double bonds<sup>6</sup>, and the reactions are assumed to involve ultimately breaking the bond and forming a carbonyl and an excited Crigiee biradical, i.e.



Two reactions are generated for each C=C bond, involving formation of the biradical from each of the two groups around the bond. Therefore, it is necessary to know both the total rate constant and the fraction of biradical formation at each of the groups around the bond.

### a. Assigned O<sub>3</sub> Rate constants

Rate constants for reaction with O<sub>3</sub> have been measured for most of the VOCs in the current mechanism for which O<sub>3</sub> reactions are assumed to be non-negligible. Table 16 lists the rate parameter assignments for all VOCs for which this is the case, and indicates the source of the assignments. Again, this includes all VOCs in the current mechanism, not just those whose reactions can be processed by the mechanism generation system. As with the other reactions, almost all of the assignments are based on recommendations from various Atkinson reviews (Atkinson and Carter, 1984; Atkinson, 1994, 1997a).

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<sup>6</sup> Reactions of O<sub>3</sub> with alkynes are included as assigned reactions for special reactants (see Section II.B.5.d), but are not automatically generated by the system.

Table 16. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with O<sub>3</sub> in the present mechanism.

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
<u>Alkanes</u>							
Ethene	ETHENE	1.68e-18	9.14e-15	5.127	1	1.68e-18	0%
Propene	PROPENE	1.05e-17	5.51e-15	3.732	1	1.01e-17	-4%
1-Butene	1-BUTENE	1.00e-17	3.36e-15	3.466	1	1.01e-17	1%
Isobutene	ISOBUTEN	1.17e-17	2.70e-15	3.243	1	1.18e-17	1%
cis-2-Butene	C-2-BUTE	1.28e-16	3.22e-15	1.924	1	1.15e-16	-10%
trans-2-Butene	T-2-BUTE	1.95e-16	6.64e-15	2.104	1	1.15e-16	-41%
1-Pentene	1-PENTEN	1.04e-17	3.36e-15	3.445	2	1.01e-17	-3%
2-Methyl-1-Butene	2M-1-BUT	1.66e-17	2.70e-15	3.037	3	1.18e-17	-29%
2-Methyl-2-Butene	2M-2-BUT	4.08e-16	2.87e-15	1.162	4	3.48e-16	-15%
3-Methyl-1-Butene	3M-1-BUT	1.14e-17	3.36e-15	3.388	2	1.01e-17	-12%
1-Hexene	1-HEXENE	1.14e-17	3.36e-15	3.388	2	1.01e-17	-12%
Cis-3-Hexene	C-3-C6E	1.53e-16	3.22e-15	1.816	5	1.15e-16	-25%
Trans-3-Hexene	T-3-C6E	1.74e-16	6.64e-15	2.170	6	1.15e-16	-34%
2-Methyl-1-Pentene	2M1-C5E	1.55e-17	2.70e-15	3.075	3	1.18e-17	-24%
3-Methyl-1-Pentene	3M1-C5E	5.12e-18	3.36e-15	3.867	2	1.01e-17	97%
4-Methyl-1-Pentene	4M1-C5E	9.57e-18	3.36e-15	3.494	2	1.01e-17	6%
Cis-3-Methyl-2-Hexene	C3M2-C5E	4.56e-16	2.87e-15	1.096	4	3.48e-16	-24%
Trans 3-Methyl-2-Hexene	T3M2-C5E	5.66e-16	2.87e-15	0.967	4	3.48e-16	-39%
2,3-Dimethyl-1-Butene	23M1-BUT	1.35e-17	2.70e-15	3.160	3	1.18e-17	-12%
3,3-Dimethyl-1-Butene	33M1-BUT	5.43e-18	3.36e-15	3.832	2	1.01e-17	86%
2,3-Dimethyl-2-Butene	23M2-BUT	1.14e-15	3.03e-15	0.584	1	6.74e-16	-41%
2-Ethyl-1-Butene	2E1-BUT	1.35e-17	2.70e-15	3.160	3	1.18e-17	-12%
1-Heptene	1-HEPTEN	1.25e-17	3.36e-15	3.337	2	1.01e-17	-19%
2,3,3-trimethyl-1-Butene	233M1BUT	8.63e-18	2.70e-15	3.426	3	1.18e-17	37%
1-Octene	1-OCTENE	1.45e-17	3.36e-15	3.246	2	1.01e-17	-30%
Cis-4-Octene	C-4-C8E	9.73e-17	3.22e-15	2.086	5	1.15e-16	18%
Trans-4-Octene	T-4-C8E	1.44e-16	6.64e-15	2.285	6	1.15e-16	-20%
Trans 2,5-Dimethyl 3-Hexene	T25M3C6E	4.24e-17	6.64e-15	3.013	6	1.15e-16	171%
Trans 2,2-Dimethyl 3-Hexene	T22M3C6E	4.34e-17	6.64e-15	2.998	6	1.15e-16	165%
2,4,4-trimethyl-2-Pentene	244M2C5E	1.43e-16	2.87e-15	1.788	4	3.48e-16	144%
3-Methyl-2-Isopropyl-1-Butene	3M2I1C4E	3.45e-18	2.70e-15	3.972	3	1.18e-17	242%
1-Decene	1-C10E	9.67e-18	3.36e-15	3.488	2	1.01e-17	4%
Cis-5-Decene	C-5-C10E	1.23e-16	3.22e-15	1.948	5	1.15e-16	-6%
3,4-Diethyl-2-Hexene	34E2-C6E	4.39e-18	2.87e-15	3.864	4	3.48e-16	(large)
Cyclopentene	CYC-PNTE	5.61e-16	1.80e-15	0.696	1	1.15e-16	-79%
1-Methyl cyclohexene	1M-CC5E	6.76e-16	2.70e-15	0.825	3	3.48e-16	-49%
Cyclohexene	CYC-HEXE	8.33e-17	2.88e-15	2.112	1	1.15e-16	38%
1-Methyl Cyclohexene	1M-CC6E	1.68e-16	2.87e-15	1.690	4	3.48e-16	107%
4-Methyl Cyclohexene	4M-CC6E	8.40e-17	2.88e-15	2.107	7	1.15e-16	37%

Table 16 (continued)

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
1,2-Dimethyl Cyclohexene	12M-CC6E	2.11e-16	3.03e-15	1.589	8	6.74e-16	220%
1,3-Butadiene	13-BUTDE	6.64e-18	1.34e-14	4.537	1		
Isoprene	ISOPRENE	1.34e-17	7.86e-15	3.802	1		
a-Pinene	A-PINENE	8.80e-17	1.01e-15	1.455	1		
3-Carene	3-CARENE	3.78e-17	1.01e-15	1.958	9		
b-Pinene	B-PINENE	1.54e-17	1.01e-15	2.493	9		
Sabinene	SABINENE	8.74e-17	1.01e-15	1.459	9		
d-Limonene	D-LIMONE	2.04e-16	3.71e-15	1.729	10		
2-(Cl-methyl)-3-Cl-Propene	CL2IBUTE	3.90e-19			11		
Styrene	STYRENE	1.71e-17			12		
<u>Alkynes</u>							
Acetylene	ACETYLEN	8.61e-21	2.00e-14	8.739	13		
Methyl Acetylene	ME-ACTYL	1.56e-20	1.00e-14	7.970	14		
Ethyl Acetylene	ET-ACTYL	2.15e-20	1.00e-14	7.780	14		
2-Butyne	2-BUTYNE	2.15e-20	1.00e-14	7.780	15		
Methylvinyl ketone	MVK	4.74e-18	7.51e-16	3.020	12		
Methacrolein	METHACRO	1.19e-18	1.36e-15	4.200	12		
Isoprene Product #1	IP-MHY1	1.00e-17			16		
Isoprene Product #2	IP-MHY2	1.00e-17			16		
Isoprene Product #3	IP-HMY	1.00e-17			16		
Hydroxy Methacrolein	HOMACR	1.19e-18	1.36e-15	4.200	17		
Crotonaldehyde	CROTALD	9.00e-19			11		
Acrolein	ACROLEIN	3.07e-19	1.36e-15	5.006	18		

References

- 1 Rate constant expression recommended by Atkinson (1997a)
- 2 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for 1-butene.
- 3 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for isobutene.
- 4 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as the average of those for isobutene and 2,3-dimethyl-2-butene.
- 5 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for cis-2-butene.
- 6 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for trans-2-butene.
- 7 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for cyclohexene.
- 8 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for 2,3-dimethyl-2-butene.
- 9 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the same as for a-pinene.

Table 16 (continued)

References (continued)

- 10 T=298K rate constant recommended by Atkinson (1997a). Temperature dependence estimated by assuming the A factor is the sum of those for  $\alpha$ -pinene and isobutene.
- 11 Rate constant recommended by Atkinson and Carter (1984)
- 12 Rate constant recommended by Atkinson (1994).
- 13 T=298K rate constant is from Atkinson and Aschmann (1984), as recommended by IUPAC (Atkinson et al, 1999). The temperature dependence is estimated based on assuming the A factor is roughly twice that for O<sub>3</sub> + ethylene.
- 14 T=298K rate constant is from Atkinson and Aschmann (1984). The temperature dependence is estimated based on assuming the A factor is roughly twice that for O<sub>3</sub> + propene.
- 15 Assumed to have approximately the same rate constant as 1-butyne, based on data given by Atkinson and Carter (1984).
- 16 Rate constant estimated by Carter and Atkinson (1996)
- 17 Estimated to have the same rate constant as methacrolein (Carter and Atkinson, 1996)
- 18 Rate constant at 298K of 2.9e-19 recommended by Atkinson (1994). Activation energy assumed to be the same as used for methacrolein.

**b. Estimated Total Rate Constants**

As discussed by Atkinson and Carter (1984), ozone + alkene rate constants tend to be quite variable depending on the structure of the compound, even if grouped according to the number of substituents on each side of the double bond. This is shown on Figure 2, which shows a comparison of the T=300K rate constants for the various monoalkenes tabulated by Atkinson (1997a), with a separate plot for each type of double bond structure. Note that cyclohexenes (which tend to have higher O<sub>3</sub> rate constants) and terpenes (whose structures the mechanism generation system cannot presently handle) are not shown. It can be seen that there is variability in the rate constants, particularly for the 1,1-disubstituted compounds. It is interesting to note that the more highly branched compounds tend to have the lowest rate constants, suggesting that steric effects may be important.

Fortunately, measured O<sub>3</sub> rate constants are available for most of the alkenes that are important in current emissions, which tend to be the lower molecular weight compounds. However, it is still necessary to have a method to estimate rate constants for those compounds where no data are available, even if it is uncertain. For this purpose, we use the average of the rate constants for the reactions at the various types of double bonds, as shown on Figure 2, and as summarized on Table 17. Table 16, above, shows the discrepancies between the experimental and estimated values for all the alkenes in the current mechanism. The anomalously low value for 3,4-dietyl-2-hexene (which may be low because of steric hindrance) was not used when computing the average for  $-\text{CH}=\text{C}<$ . Although there is variability, the averages are probably appropriate as best estimates for compounds whose rate constants are not known, at least for use by the mechanism generation system at its current state of development. Obviously, compounds with large steric effects need to be estimated on a case-by-case basis.

Figure 2. Comparison of O<sub>3</sub> + alkene rate constants for alkenes with the same configurations of constituents about the double bond.

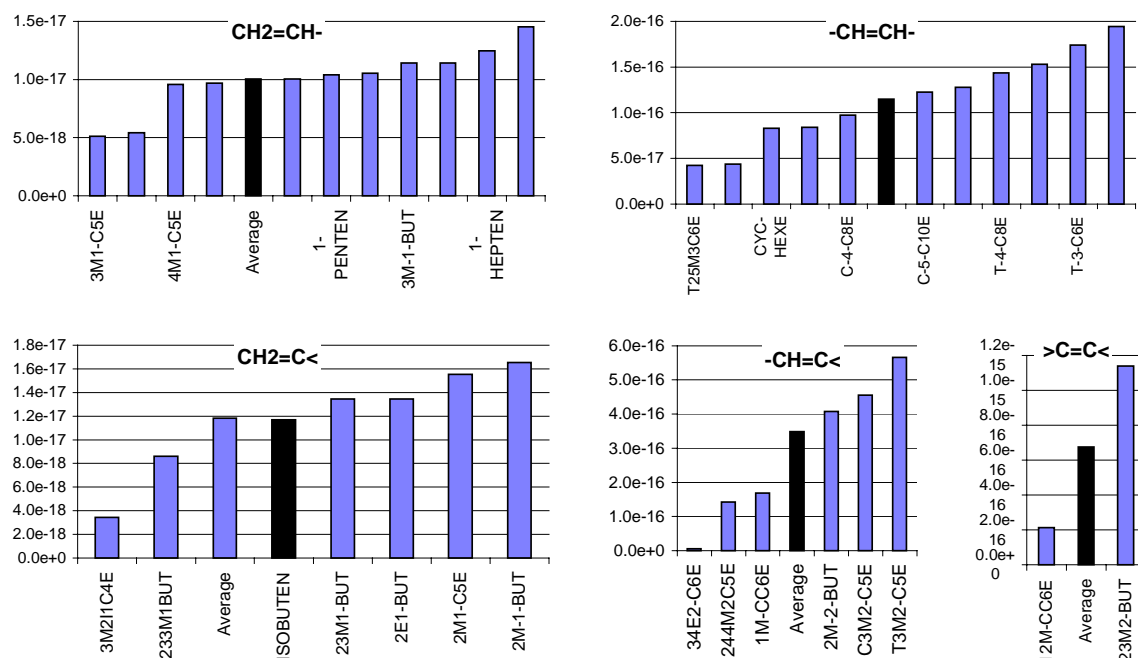


Table 17. Summary of rate constant estimates for reactions of O<sub>3</sub> at alkene groups.

Groups		Estimated Total Rate Constant (300K) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )
CH <sub>2</sub> =CH-	1.01e-17	Average of 300K values for propene, 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene, 3-methyl-1-pentene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene, 1-heptene, 1-octene, and 1-decene (Atkinson, 1997a).
CH <sub>2</sub> =C<	1.18e-17	Average of 300K values for isobutene, 2-methyl-1-butene, 23-dimethyl-1-butene, 2-ethyl-1-butene, 2-methyl-1-pentene, 2,3,3-trimethyl-1-butene, 3-methyl-2-isopropyl-1-butene, and 3,4-diethyl-2-hexene (Atkinson, 1997a).
-CH=CH-	1.15e-16	Average of 300K values for trans-2-butene, cis-2-butene, trans-3-hexene, cis-3-hexene, cis-4-octene, trans-4-octene, trans 2,5-dimethyl 3-hexene, trans 2,2-dimethyl 3-hexene, cis-5-decene, cyclohexene, and 4-methyl cyclohexene (Atkinson, 1997a).
-CH=C<	3.48e-16	Average of 300K values for 2-methyl-2-butene, cis-3-methyl-2-hexene, trans 3-methyl-2-hexene, 2,4,4-trimethyl-2-pentene, and 1-methyl cyclohexene (Atkinson, 1997a).
>C=C<	6.74e-16	Average of 300K values for 2,3-dimethyl-2-butene and 1,2-dimethyl cyclohexene (Atkinson, 1997a).



### **c. Branching Ratios for Biradical Formation**

Since the biradical and carbonyl formation in the initial  $O_3$  reaction can occur on two different positions in unsymmetrical molecules, it is necessary to specify their relative importances. Information concerning this can be obtained from the measured yields of the primary carbonyl products, which are summarized by Atkinson (1997a). The averages of the primary yield data given by Atkinson (1997a) are summarized on Table 18 through Table 20 for the olefins with the various types of unsymmetrical groups where such data are available. In most cases the sum of these primary product yields are within experimental uncertainty of unity, indicating that these products account for the total  $O_3$  + alkene reactions. (The main exceptions are propene [Table 18] and isobutene [Table 19], where higher than unit yields can be attributed to formaldehyde formation from the secondary reactions of the excited biradical.) Atkinson (1997a) also summarizes carbonyl yield data for symmetrical alkenes (not shown here), and in most of those cases near-unit yields of the expected single carbonyl product are observed.

Table 18. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O<sub>3</sub> with alkenes with CH<sub>2</sub>=CH- groups.

	Experimental			Estimated		OH Yield		
	HCHO	RCHO	Sum	RCHO	Error	Expt.	Est'd.	Error
<u>CH<sub>2</sub>=CH- Average</u>		<u>0.54</u>		<u>0.5</u>	<u>-8%</u>			<u>-6%</u>
Propene	0.71	0.48	1.20	0.5	3%	0.33	0.32	-3%
1-Butene	0.63	0.35	0.98	0.5	30%	0.41	0.32	-22%
1-Pentene	0.55	0.52	1.07	0.5	-4%	0.37	0.32	-14%
1-Hexene	0.54	0.53	1.07	0.5	-5%	0.32	0.32	0%
1-Heptene	0.52	0.55	1.07	0.5	-9%	0.27	0.32	19%
1-Octene	0.50	0.51	1.01	0.5	-2%	0.32	0.32	0%
1-Decene	0.53	0.49	1.02	0.5	2%			
3-Methyl-1-Butene	0.50	0.51	1.01	0.5	-2%			
3-Methyl-1-Pentene	0.39	0.63	1.03	0.5	-26%			
4-Methyl-1-Pentene	0.44	0.71	1.15	0.5	-41%			
3,3-Dimethyl-1-Butene	0.32	0.67	0.99	0.5	-34%			
Cyclohexene						0.68	0.52	-24%

Table 19. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O<sub>3</sub> with alkenes with CH<sub>2</sub>=C< groups.

	Experimental			Estimated		OH Yield		
	HCHO	R-CO-R'	Sum	R-CO-R'	Error	Expt.	Calc	Error
<u>CH<sub>2</sub>=C&lt; Average</u>		<u>0.34</u>		<u>0.333</u>	<u>-2%</u>			<u>4%</u>
Isobutene	0.98	0.32	1.29	0.333	4%	0.84	0.71	-16%
2-Methyl-1-Butene	0.64	0.28	0.92	0.333	16%	0.83	0.71	-15%
2-Methyl-1-Pentene	0.62	0.32	0.94	0.333	3%			
2-Ethyl-1-Butene	0.49	0.30	0.80	0.333	9%			
2,3-Dimethyl-1-Butene	0.72	0.38	1.10	0.333	-14%	0.5	0.71	41%
2,3,3-trimethyl-1-Butene	0.64	0.35	0.99	0.333	-6%			
3-Methyl-2-Isopropyl-1-Butene	0.61	0.43	1.03	0.333	-28%			

Table 20. Experimental and estimated yields of primary carbonyl products and OH radicals from the reactions of O<sub>3</sub> with alkenes with -CH=C< groups.

	Experimental			Estimated		OH Yield		
	RCHO	R-CO-R'	Sum	R-CO-R'	Error	Expt.	Calc	Error
<u>-CH=C&lt; Average</u>		<u>0.27</u>		<u>0.3</u>	<u>10%</u>			<u>-8%</u>
2-Methyl-2-Butene	0.72	0.34	1.05	0.3	-13%	0.91	0.84	-8%
2,4,4-Trimethyl-2-Pentene	0.84	0.19	1.03	0.3	38%			
3,4-Diethyl-2-Hexene	0.71	0.29	0.99	0.3	4%			
1-Methyl Cyclohexene						0.90	0.84	-7%

For alkenes with  $\text{CH}_2=\text{CH}-$  groups, Table 18 indicates that the data for most alkenes are consistent with assuming equal probability for each of the two possible reaction modes. This is therefore assumed when generating  $\text{O}_3$  reaction mechanisms for all alkenes of this type. The major exception appears to be highly branched compounds such as 3,3-dimethyl-1-butene, where steric effects may tend to reduce biradical formation on the most substituted side. Since the current mechanism generation system is not capable of assessing steric effects, such compounds need to be handled on a case-by-case basis. However, present assignments are not made for such compounds because they are not important in current emissions inventories. The average error in assuming equal splits for the compounds where data are available is less than 10%, and the absolute value of the percentage error is less than 15%.

For alkenes with  $\text{CH}_2=\text{C}<$  groups, Table 19 indicates that the data are more consistent with assuming that fragmentation to formaldehyde + the disubstituted is essentially twice as probable as fragmentation to the ketone +  $\text{HCHO}_2$  in essentially all cases. Steric effects appear to be less important in affecting this generalization, as suggested by the data for 2,3,3-trimethyl-1-butene. Therefore, the  $\text{O}_3$  reactions of alkenes of this type are generated based on assuming that ketone +  $\text{HCHO}_2$  formation occurs 33.3% of the time, as indicated on the table. This gives an average error of less than 5% and an average absolute percentage error of less than 15%.

For alkenes with  $-\text{CH}=\text{C}<$  groups, Table 20 indicates that aldehyde + disubstituted biradical formation occurs a larger fraction of the time than formation of the ketone + the monosubstituted biradical, but the limited data indicate somewhat variable ratios. For mechanism estimation and generation purposes, we assume that ketone + monosubstituted biradical formation occurs 30% of the time, as indicated on the table. This gives an average error of 10% and an average absolute percentage error of slightly less than 20% for the three compounds that were studied.

Atkinson (1997a) gives no information concerning primary carbonyl yields from unsymmetrical molecules with  $-\text{CH}=\text{CH}-$  or  $>\text{C}=\text{C}<$  groups – only data for symmetrical molecules are tabulated. For estimation and mechanism generation purposes, we assume equal probability for the two modes of reaction in such cases. The data for the other unsymmetrical molecules indicate that this is probably a good approximation, with the possible exception of molecules that are highly branched on one side where steric effects may come into play.

Table 18 through Table 20 also show measured yields of OH radicals, which are believed to be formed from secondary radicals of the biradical intermediates (see Section ??). If it is assumed that the OH yields from the excited  $\text{HCHO}_2$ ,  $\text{RCHO}_2$ , and  $\text{RR}'\text{CO}_2$  biradicals are independent of the molecule from which they are formed and on the nature of the “R” or “R'” substituents, then these OH yields should be consistent with the assumed branching ratios and the OH yields assumed for the various types of biradicals. As discussed in Section ??, the current mechanism assumes that OH yields from excited  $\text{HCHO}_2$ ,  $\text{CH}_3\text{CHO}_2$ , are respectively 12%, 52%, and 100%, based primarily on recommendations and data discussed by Atkinson (1997a). The “Calc'd” OH yields on Table 18 through Table 20 show the yields for the various molecules derived based on these assumptions, where they can be compared with the experimental data. In most cases these are consistent with the experimental data, with the percentage errors being no greater than those for the estimated carbonyl yields. Therefore, the estimates based on carbonyl yields and OH yields are self-consistent. However, as discussed in Section ??, the experimental and estimated OH yields for the  $\text{C}_{4+}$  1-alkenes are not consistent with the environmental chamber reactivity data for these compounds, and lower adjusted OH yields have to be used for the purpose of reactivity predictions. However, these adjustments do not affect the assumed branching ratios for the initial  $\text{O}_3$  + alkene reactions.

#### **d. Assigned Mechanisms for Initial O<sub>3</sub> Reactions**

As with the other reactions discussed above, explicit assignments are used for the initial reactions for those VOCs where estimates cannot be made, where available experimental data indicate the estimates are inappropriate, or where alternative estimates are used. The explicitly assigned branching ratios for the initial O<sub>3</sub> reactions that are currently incorporated in the system are summarized on Table 21, along with the basis for the various assignments that are used.

Table 21. Assigned mechanisms for the reactions of O<sub>3</sub> with compounds for which estimates could not be made, or where experimental data or other considerations indicate that the general estimates may not be appropriate.

Reactant and Products	Factor	Documentation
<u>1,3-Butadiene [CH<sub>2</sub>=CH-CH=CH<sub>2</sub>]</u>		
HCHO + CH <sub>2</sub> =CH-CHOO[excited]	50.0%	Estimated mechanism.
CH <sub>2</sub> =CH-CHO + CH <sub>2</sub> OO[excited]	50.0%	Estimated mechanism.
<u>Isoprene [CH<sub>2</sub>=CH-C(CH<sub>3</sub>)=CH<sub>2</sub>]</u>		
HCHO + CH <sub>2</sub> =CH-COO[excited]-CH <sub>3</sub>	20.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCHO + CH <sub>2</sub> =C(CHOO[excited])-CH <sub>3</sub>	20.0%	See above.
CH <sub>2</sub> =C(CH <sub>3</sub> )-CH <sub>3</sub> + CH <sub>2</sub> OO[excited]	39.0%	See above.
CH <sub>2</sub> =CH-CO-CH <sub>3</sub> + CH <sub>2</sub> OO[excited]	16.0%	See above.
O <sub>2</sub> + *C(CH=CH <sub>2</sub> )(CH <sub>3</sub> )-CH <sub>2</sub> -O-*	2.5%	See above.
O <sub>2</sub> + *CH(C(CH <sub>3</sub> )=CH <sub>2</sub> )-CH <sub>2</sub> -O-*	2.5%	See above.
<u>Acetylene [HC::CH]</u>		
HCO-CHOO[excited]	100.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. [a]
<u>Methyl Acetylene [HC::C-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -COO[excited]-CHO	50.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. Equal probability of formation of each possible isomer is assumed. [a]
CH <sub>3</sub> -CO-CHOO[excited]	50.0%	See above.
<u>Ethyl Acetylene [HC::C-CH<sub>2</sub>-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -CH <sub>2</sub> -COO[excited]-CHO	50.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. Equal probability of formation of each possible isomer is assumed. [a]
CH <sub>3</sub> -CH <sub>2</sub> -CO-CHOO[excited]	50.0%	See above.
<u>2-Butyne [CH<sub>3</sub>-C::C-CH<sub>3</sub>]</u>		
CH <sub>3</sub> -CO-COO[excited]-CH <sub>3</sub>	100.0%	The initially formed primary ozonide is assumed to rearrange to the Crigiee biradical via an O-O bond scission. [a]
<u>Methacrolein [CH<sub>2</sub>=C(CH<sub>3</sub>)-CHO]</u>		
HCHO + CH <sub>3</sub> -COO[excited]-CHO	10.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH <sub>3</sub> -CO-CHO + CH <sub>2</sub> OO[excited]	90.0%	See above
<u>Hydroxy Methacrolein [CH<sub>2</sub>=C(CH<sub>3</sub>)-CH<sub>2</sub>-OH]</u>		
HCO-CO-CH <sub>2</sub> -OH + CH <sub>2</sub> OO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCHO + HCO-COO[excited]-CH <sub>2</sub> -OH	10.0%	See above
<u>Isoprene Product #1 [CH<sub>3</sub>-C(CH<sub>3</sub>)=CH-CH<sub>2</sub>-OH]</u>		
CH <sub>3</sub> -CO-CHO + HO-CH <sub>2</sub> -CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH <sub>2</sub> -OH + CH <sub>3</sub> -COO[excited]-CHO	10.0%	See above
<u>Isoprene Product #2 [CH<sub>3</sub>-C(CH<sub>3</sub>)=CH-CH<sub>2</sub>-OH]</u>		
CH <sub>3</sub> -CO-CHO + HO-CH <sub>2</sub> -CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CH <sub>2</sub> -OH + CH <sub>3</sub> -COO[excited]-CHO	10.0%	See above

Table 21 (continued)

Reactant and Products	Factor	Documentation
<u>Isoprene Product #3 [HCO-CH=C(CH<sub>3</sub>)-CH<sub>2</sub>-OH]</u>		
CH <sub>3</sub> -CO-CH <sub>2</sub> -OH + HCO-CHOO[excited]	90.0%	Mechanism of Carter and Atkinson (1996) is assumed.
HCO-CHO + CH <sub>3</sub> -COO[excited]-CH <sub>2</sub> -OH	10.0%	See above
<u>Methylvinyl ketone [CH<sub>2</sub>=CH-CO-CH<sub>3</sub>]</u>		
HCHO + CH <sub>3</sub> -CO-CHOO[excited]	5.0%	Mechanism of Carter and Atkinson (1996) is assumed.
CH <sub>3</sub> -CO-CHO + CH <sub>2</sub> OO[excited]	95.0%	See above
[a] Although the biradical excitation energies are almost certainly different from those formed in the reactions of O <sub>3</sub> with acroleins, because of lack of available information it is assumed to react to form the same products, and thus is represented by the same species.		

## 6. Reactions with O<sup>3</sup>P

O<sup>3</sup>P atoms can react with compounds with C=C double bonds, forming an excited adduct that may decompose in various ways or undergo collisional stabilization. Although these reactions are generally of negligible importance under most ambient atmospheric conditions, they have been found to be non-negligible in some of the environmental chamber experiments used for mechanism evaluation, where NO<sub>2</sub> concentrations tend to be higher under ambient conditions<sup>7</sup>. They may also be non-negligible in plumes that have higher NO<sub>x</sub> concentrations than ambient. For these reasons, O<sup>3</sup>P + alkene reactions are included in the current mechanism and are supported by the mechanism generation system.

### a. Assigned O<sup>3</sup>P Rate Constants

The rate constant assignments used for the O<sup>3</sup>P reactions that are incorporated in the present mechanism are given on Table 22, where they are compared for the estimated values for those VOCs for which estimates can be made. The table also indicates the source of the rate constant assignments, which in most cases are from Atkinson (1997a).

<sup>7</sup> Reactions with O<sub>3</sub>P increase in importance as NO<sub>2</sub> concentrations increase because NO<sub>2</sub> photolysis is the primary source of O<sup>3</sup>P.

Table 22. Rate constant and temperature dependence parameter assignments used for reactions of VOCs with O<sup>3</sup>P atoms in the present mechanism.

Compound	DMS name	k(300) (cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )	A	Ea kcal/mole	Ref	Est'd k(300) k	(diff)
<u>Alkanes</u>							
Ethene	ETHENE	7.42e-13	1.04e-11	1.574	1		
Propene	PROPENE	4.01e-12	1.18e-11	0.644	1	3.91e-12	-2%
1-Butene	1-BUTENE	4.22e-12	1.25e-11	0.648	1	5.43e-12	29%
Isobutene	ISOBUTEN	1.69e-11			2	1.36e-11	-20%
cis-2-Butene	C-2-BUTE	1.76e-11			2	1.62e-11	-8%
trans-2-Butene	T-2-BUTE	2.18e-11			2	2.04e-11	-6%
1-Pentene	1-PENTEN	4.69e-12	1.48e-11	0.686	3	5.42e-12	16%
cis-2-Pentene	C-2-PENT	1.70e-11			2	2.09e-11	23%
3-Methyl-1-Butene	3M-1-BUT	4.18e-12	1.32e-11	0.686	3	5.55e-12	33%
2-Methyl-2-Butene	2M-2-BUT	5.10e-11			2	3.62e-11	-29%
1-Hexene	1-HEXENE	4.69e-12	1.48e-11	0.686	3	7.37e-12	57%
2,3-Dimethyl-2-Butene	23M2-BUT	7.64e-11			2	5.60e-11	-27%
Cyclopentene	CYC-PNTE	2.10e-11			2	2.23e-11	6%
Cyclohexene	CYC-HEXE	2.00e-11			2	2.26e-11	13%
1-Methyl Cyclohexene	1M-CC6E	9.00e-11			2	3.71e-11	-59%
1,3-Butadiene	13-BUTDE	1.98e-11			2		
Isoprene	ISOPRENE	3.60e-11			4		
a-Pinene	A-PINENE	3.20e-11			2		
3-Carene	3-CARENE	3.20e-11			2		
b-Pinene	B-PINENE	2.70e-11			2		
d-Limonene	D-LIMONE	7.20e-11			2		

#### References

- 1 Rate constant expression from Atkinson and Lloyd (1984). T=298K value is consistent with recommendation of Atkinson (1997a).
- 2 Rate constant from Atkinson (1997a). Temperature dependence is expected to be small.
- 3 T=298K rate constant from Atkinson (1997a). Activation energy estimated from propene and 1-butene, as given by Atkinson and Lloyd (1984).
- 4 Rate constant from Paulson et al (1995).

## b. Estimated O<sup>3</sup>P Rate Constants

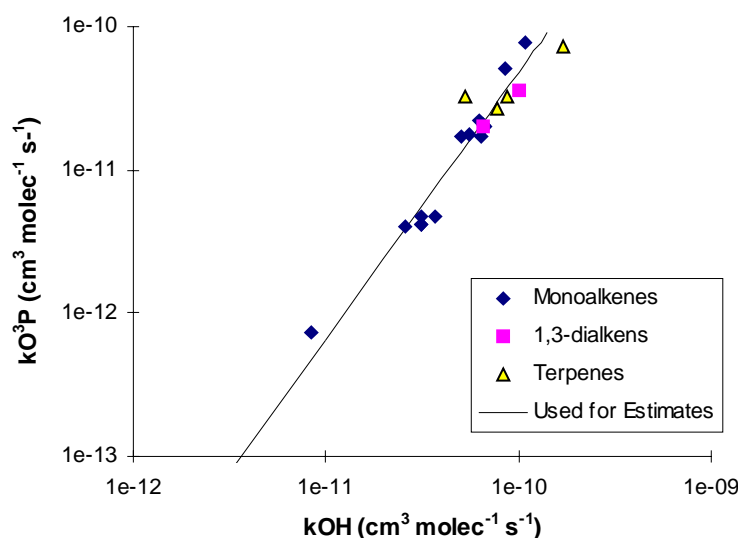
Since the reactions of alkenes with O<sup>3</sup>P and OH radicals are both believed to involve primarily addition to the double bond, one might expect the rate constants for these reactions to be correlated. This is indeed the case for most of the alkenes where both rate constants have been measured, as is shown on Figure 3, which gives a log-log plot of O<sup>3</sup>P and OH radical rate constants for the alkenes listed on Table 22. The line shows the least squares fit for the log-log plot for the monoalkenes, which was used for the purpose of estimating O<sup>3</sup>P rate constants for those alkenes for which data are not available. This is given by:

$$\ln(k\text{O}^3\text{P}) = 19.160 + 1.864 \ln(k\text{OH}) \quad (\text{II})$$

where  $k\text{O}^3\text{P}$  and  $k\text{OH}$  are the O<sup>3</sup>P and OH radical rate constants in  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . (Note that the third digits are significant since they are being used to compute logarithms.) Although the dialkenes and the terpenes are not used when deriving this fit, Table 22 and Figure 3 show that the above equation performs reasonably well in predicting their rate constants in most cases. Including the terpenes and dialkenes, the average discrepancy is around 25%, and all the discrepancies in all cases except for d-limonene are less than 60%.

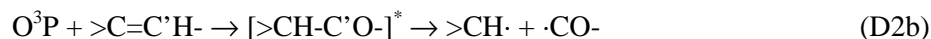
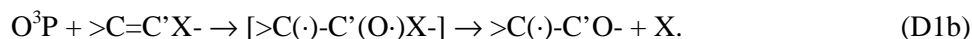
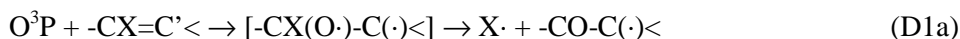
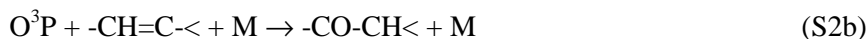
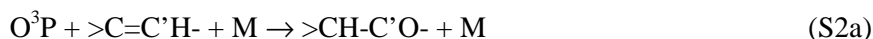


Figure 3. Plot of OH radical vs. O<sup>3</sup>P rate constants for VOCs in the mechanism where both rate constants are available. Rate constants are for T=300K.



### c. Estimated Mechanisms for O<sup>3</sup>P Reactions

The mechanisms for the reactions of O<sup>3</sup>P with the simpler alkenes have been recently reviewed by Atkinson (1997a), though the discussion there is based primarily on the earlier review of Atkinson and Lloyd (1984). The reaction presumably proceeds by O adding to the double bond forming an excited oxide, which can either be collisionally stabilized, undergo a 1,2-H shift to a carbonyl compound and then be stabilized, or decompose in various ways. Neglecting reactions requiring pentavalent transition states that are chemically unreasonable (e.g., formation of isobutyraldehyde from O<sup>3</sup>P + 2-butenes), the alternative reaction routes given by Atkinson and Lloyd (1984) and Atkinson (1997a) can be classified as follows:



Where, for unsymmetrical molecules, C' refers to the carbon that has the greater number of substituents.

Branching ratios estimated or interpolated based on these data are given in Table 23, where the branching ratio designations used are as indicated above, and footnotes indicate the source of the estimated mechanisms. Note that these ratios are applicable to one atmosphere total pressure only –

the mechanism generation system currently does not support predicting the effects of total pressure on these yields<sup>8</sup>. Atkinson (1997a) and Atkinson and Lloyd (1994) gave no recommendations for compounds of with  $\text{CH}_2=\text{C}<$ ,  $-\text{CH}=\text{C}<$ , or  $>\text{C}=\text{C}<$ , and highly approximate estimates are made based on considerations of data given by Atkinson and Lloyd (1994) for other compounds<sup>9</sup>. As indicated on the table, stabilization is assumed to become increasingly important for higher molecular weight compounds, and to dominate for  $\text{C}_{7+}$  alkenes.

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<sup>8</sup> Ignoring these pressure dependences is unlikely to introduce significant errors in tropospheric simulations because  $\text{NO}_2$  concentrations are expected to be sufficiently low at higher altitudes that reactions of  $\text{O}^3\text{P}$  with alkenes is expected to be negligible.

<sup>9</sup> It is probable that improved estimates could be made for some of these compounds by reviewing the product data literature. This review was not carried out because of the relatively low importance of these  $\text{O}^3\text{P}$  reactions in most atmospheric simulations, and because in any case the branching ratios had to be revised to fit the chamber data.

Table 23. Estimated branching ratios for the reactions of O<sup>3</sup>P with alkenes, based on the recommendations of Atkinson (1997a) and Atkinson and Lloyd (1984). Note that these ratios are not used in the final mechanism because of unsatisfactory results when simulating environmental chamber experiments.

Compound	Branching Ratio							Notes
	S1	S2a	S2b	D1a	D1b	D2a	D2b	
<u>CH2=CH2</u>								
Ethene	0%	0%		60%		40%		1
<u>CH2=CH-</u>								
Propene	30%	30%	0%	20%	0%	20%	0%	2
1-Butene	45%	40%	0%	15%	0%	0%	0%	2
C5 Alkenes	50%	45%	0%	5%	0%	0%	0%	3
C6+ Alkenes	55%	45%	0%	0%	0%	0%	0%	3
<u>CH2=C&gt;</u>								
Isobutene	40%	-	30%	0%	15%	15%	-	4
C5 Alkenes	50%	-	38%	0%	6%	6%	-	3
C6 Alkenes	56%	-	40%	0%	2%	2%	-	3
C7+ Alkenes	60%	-	40%	0%	0%	0%	-	3
<u>-CH=CH-</u>								
2-Butenes	50%	20%		30%		0%		5
C5 Alkenes	64%	24%		12%		0%		3
C6 Alkenes	72%	24%		4%		0%		3
C7+ Alkenes	76%	24%		0%		0%		3
<u>-CH=C&lt;</u>								
2-Methyl-2-Butene	50%	-	38%	6%	6%	0%	-	4
C6 Alkenes	56%	-	40%	2%	2%	0%	-	3
C7+ Alkenes	60%	-	40%	0%	0%	0%	-	3
<u>&gt;C=C&lt;</u>								
2,3-Dimethyl-2-Butene	96%	-		2%	2%	-		4
C7+ Alkenes	100%	-		0%	0%	-		3

- 1 Based on Atkinson (1997a) recommendation, ignoring ketene formation, which is lumped with the D2 decomposition route
- 2 Based on Atkinson (1997a) and Atkinson and Lloyd (1984) recommendation. Numbers rounded to nearest 5%
- 3 Based on extrapolating from data for lower molecular weight alkenes, assuming that stabilization will increase with the size of the molecule increases.
- 4 Estimated based on recommended mechanisms given by Atkinson and Lloyd (1994) for other alkenes.
- 5 Based on the Atkinson (1997a) and Atkinson and Lloyd (1984) recommendation, with the chemically unreasonable 20% CH<sub>3</sub> shift represented by increasing oxide formation and

Although the branching ratios shown on Table 23 represent our current best estimates based on available product data (Atkinson, 1997a), as discussed in Section ?? it was found that using these branching ratios gave unsatisfactory results when conducting model simulations of the available chamber database. This was found to be the case even after reasonable adjustment of the other uncertain parameters in the mechanism that affect radical initiation or termination processes. In order to fit the data, it was necessary to assume much lower radical yields from these  $O^3P$  reactions, i.e., that stabilization is much more important than indicated by the available product data. In particular, the model significantly overpredicts the reactivity of 1-butene and 1-hexene if any radical formation in the  $O^3P$  reaction is assumed, and consistent fits to the chamber data cannot be obtained unless it is assumed that radical formation from  $O^3P$  + propene is also negligible. In addition, assuming only 50% fragmentation in the  $O^3P$  + ethene rather than the recommended 100% removes biases in the simulation of the large database of ethene experiments. See Section ?? for a more complete discussion of these results.

The reason for this apparent inconsistency between the chamber data and the  $O^3P$  branching ratios indicated by the available product data is unknown, and needs to be investigated. Although  $O^3P$  reactions are not important under most atmospheric conditions, they are non-negligible in many of the chamber experiments used for mechanism evaluation, and using incorrect  $O^3P$  + alkene mechanisms may compensate for other errors in the mechanism. However, no reasonable adjustments of the other uncertainties in the alkene mechanisms that involve radical initiation/termination processes (such as nitrate yields from the peroxy radicals formed in the OH reaction, radical yields from the biradicals formed in the  $O_3$  reaction, or radical generation in the alkene +  $NO_3$  reactions) could be found to give satisfactory fits to the chamber data using the recommended  $O^3P$  branching ratios. Therefore, adjusted branching ratios, assuming no radical formation from  $C_{3+}$  alkenes and assuming only 50% fragmentation from ethene, are used in the current version of the mechanism that is developed in this work. These adjusted yields are given on Table 24.

Table 24. Adjusted branching ratios for the reactions of O<sup>3</sup>P with alkenes that are found to give best fits to the available chamber database and are used in the final version of the mechanism developed in this work.

Groups	Branching Ratio				
	S1	S2a	S2b	D1a+D1b	D2a+D2b
CH <sub>2</sub> =CH <sub>2</sub>	25%	25%		20%	30%
CH <sub>2</sub> =CH-	55%	45%	0%	0%	0%
CH <sub>2</sub> =C>	60%	-	40%	0%	0%
-CH=CH-	76%	24%		0%	0%
-CH=C<	60%	-	40%	0%	0%
>C=C<	100%	-		0%	-

#### d. Assigned Mechanisms for Dialkenes

Although it is expected that the reactions of O<sup>3</sup>P with alkynes are unimportant and therefore are ignored in the mechanism, their reactions with isoprene and 1,3-butadiene may be non-negligible under some conditions, and need to be specified explicitly. The assigned O<sup>3</sup>P mechanisms for these compounds are shown on Table 25. The O<sup>3</sup>P + isoprene mechanism is based on that of Carter and Atkinson (1996), and the mechanism for 1,3-butadiene is assumed to be analogous. The current system does not have assigned mechanisms for any other VOCs.

Table 25. Assigned mechanisms for the reactions of O<sup>3</sup>P atoms with the dialkenes in the current mechanism.

Reactant and Products	Factor	Documentation
<u>Isoprene [CH<sub>2</sub>=CH-C(CH<sub>3</sub>)=CH<sub>2</sub>]</u>		
*C(CH=CH <sub>2</sub> )(CH <sub>3</sub> )-CH <sub>2</sub> -O-*	50.0%	As assumed by Carter and Atkinson (1996). Products represented by epoxides. Most of the reaction is assumed to occur at the more substituted position.
*CH(C(CH <sub>3</sub> )=CH <sub>2</sub> )-CH <sub>2</sub> -O-*	25.0%	See above.
CH <sub>2</sub> =CH-CO-CH <sub>2</sub> . + CH <sub>3</sub> .	25.0%	Fragmentation mechanism and yield as assumed by Carter and Atkinson (19896). Approximately 25% radical yield also necessary to obtain satisfactory fit to data with updated mechanism.
<u>1,3-Butadiene [CH<sub>2</sub>=CH-CH=CH<sub>2</sub>]</u>		
*CH(CH=CH <sub>2</sub> )-CH <sub>2</sub> -O-*	75.0%	Assumed to be analogous to the isoprene mechanism of Carter and Atkinson (1996). Products represented by epoxides.
CH <sub>2</sub> =CH-CH[.] -CHO + H.	25.0%	Analogous to the fragmentation mechanism in the isoprene system as assumed by Carter and Atkinson (1996).

## 7. Photolysis Reactions

Although the previous mechanism represented all aldehydes and ketones using the lumped molecule approach, this approach has proven to be unsatisfactory for the higher ketones (Carter et al, 1999a) and is therefore not used in this mechanism. Instead, specific mechanistic assignments are made for these compounds, based on generated mechanisms for their reactions with OH radicals, NO<sub>3</sub> (for aldehydes), and photolyses. Specific mechanistic assignments are also made for the OH radical and photolysis reactions of organic nitrates, which were used for determining the lumped organic nitrate mechanism as discussed in Section II.A.3.b. The estimation and generation of their initial reactions with OH radicals and NO<sub>3</sub> were discussed above. This section discusses the estimation and generation of their initial photolysis reactions.

Photolysis rates for the aldehydes and organic nitrates are estimated by assuming that they have the same absorption cross sections and quantum yields as the most chemically similar lower molecular weight analogue that is in the base mechanism. In the case of the ketones, it is assumed that the overall quantum yield decreases with the size of the molecule, based on overall quantum yields which give best fits of model simulations to environmental chamber data for methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, and methyl amyl ketone (see Section ??). The specific assignments are as summarized on Table 26, along with footnotes indicating the derivations of the assignments and the groups used by the mechanism generation system to classify compounds according to photolysis type. Note that if the molecule has groups bonded to the carbonyl or nitrate groups that are different than those indicated on the table, then the system cannot currently generate photolysis reactions for compounds with that structure.

Table 26. Summary of assignments of absorption cross sections and quantum yields for carbonyl and organic nitrate photolysis reactions.

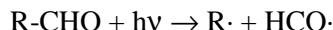
Compound Type	Phot. Set	Q.Yield	Note	Group Definition used to Determine Type
Aldehydes	C2CHO	-	1,2	-CHO groups bonded to -CH <sub>3</sub> , -CH <sub>2</sub> -, -CH< or -C<
Ketones (4 groups)	KETONE	0.15	3,4	-CO- groups bonded to -CH <sub>3</sub> , -CH <sub>2</sub> -, -CH< or -C<, with a total of 4 groups in the molecule.
Ketones (5)	KETONE	0.10	3,5	As above, but 5 groups in the molecule
Ketones (6)	KETONE	0.05	3,6	As above, but 6 groups in the molecule
Ketones (7)	KETONE	0.02	3,7	As above, but 7 groups in the molecule
Ketones (8)	KETONE	0.01	3,8	As above, but 8 groups in the molecule
Ketones (9+)	No photolysis		3,9	As above, but more than 8 groups in the molecule
Alkyl Glyoxal	MGLY_ADJ	-	1,4	-CHO- broups bonded to -CO-
Dialkyl Glyoxyl	BACL_ADJ	-	1,5	-CO- groups bonded to -CO-
Acrolein	ACROLEIN	2.0e-3	3,6	CH <sub>2</sub> =CH-CHO only.
Other Acroleins	ACROLEIN	4.1e-3	3,7	-CHO groups bonded to -CH= or >C=
Vinyl Ketone	ACROLEIN	2.1e-3	3,8	-CO- groups bonded to -CH= or >C=
Ester or Acid	No photolysis		9	-CO- or -CHO- groups bonded to -O- or -OH
Organic Nitrates	IC3ONO2	1.0	10	-ONO <sub>2</sub> groups bonded to -CH <sub>3</sub> , -CH <sub>2</sub> -, -CH< or -C<

#### Notes

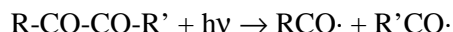
- 1 The wavelength dependent quantum yields are given with the absorption cross sections in the photolysis set. See base mechanism documentation and mechanism listing.
- 2 Assumed to have same photolysis rate as propionaldehyde.
- 3 The photolysis set gives the absorption cross sections only, which are given with the base mechanism listing. The wavelength-independent quantum yield is shown on the table.
- 4 Overall quantum yield adjusted based on model simulations of environmental chamber experiments with methyl ethyl ketone (Carter et al, 1999a).
- 5 Overall quantum yield adjusted based on model simulations of environmental chamber experiments with methyl propyl ketone (Carter et al, 1999e).
- 6 Overall quantum yield adjusted based on model simulations of environmental chamber experiments with methyl isobutyl ketone (Carter et al, 1999a).
- 7 Overall quantum yield adjusted based on model simulations of environmental chamber experiments with 2-heptanone (Carter et al, 1999e).
- 8 Estimated to have an overall quantum yield which is half that estimated for ketones with seven groups.
- 9 Photodecomposition is estimated to be unimportant for ketones with nine or more groups.
- 4 Assumed to have the same photolysis rate as methyl glyoxal.
- 5 Assumed to have the same photolysis rate as biacetyl.
- 6 Overall quantum yield adjusted to fit model simulations of O<sub>3</sub>, NO, acrolein, and formaldehyde in acrolein - NO<sub>x</sub> chamber runs ITC941, 943, and 944.
- 7 Assumed to have same photolysis rate as methacrolein. See base mechanism documentaion.
- 8 Assumed to have same photolysis rate as methyl vinyl ketone. See base mechanism documentation.
- 9 Photolysis assumed to be negligible, based on absorption cross section data given by Calvert and Pitts
- 10 All alkyl nitrates are assumed to photolyze at the same rate and with a unit quantum yield. Absorption cross sections used are those recommended by IUPAC (Atkinson et al, 1997a, 1999) for isopropyl nitrate.

### a. Default Carbonyl Photolysis Mechanisms

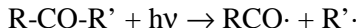
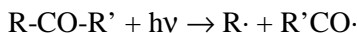
Although the actual mechanisms for the photolysis reactions of the higher molecular weight carbonyl compounds may well be more complex (Calvert and Pitts, 1966), unless information is available otherwise, it is assumed that all photolyses of carbonyls proceed by breaking the weakest CO-C bond. In the case of aldehydes (including glyoxals) this means the reaction is assumed to always proceed via



(where “R” would be R'CO in the case of glyoxals) and in the case of  $\alpha$ -dicarbonyl ketones it is assumed always to proceed via



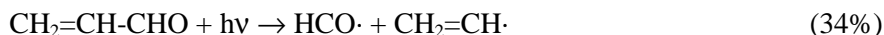
In the case of unsymmetrical ketones, two possible reactions are considered:



In this case, the pathway with the lowest estimated heat of reaction is assumed to 100% of the time, regardless of the differences between them. This gives a prediction that is consistent with the assumed photolysis mechanism for methyl ethyl ketone in the base mechanism.

### b. Unsaturated Carbonyl Photolysis

Somewhat different photolysis mechanisms are assigned for acrolein, methacrolein and methyl vinyl ketone, based on the mechanisms for the latter two given by Carter and Atkinson (1996). The base mechanism listing gives the assignments and documentation in the cases of methacrolein and MVK. In the case of acrolein, the following initial photolysis mechanism is used, which is derived by analogy to the Carter and Atkinson (1996) mechanism for methacrolein.



The subsequent reactions of the radicals or carbenes formed are discussed in the following sections.

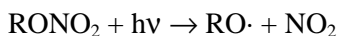
For the other unsaturated aldehydes, including specifically those used to derive the mechanism for the ISOPROD model species, the default mechanism, based on assuming 100% HCO $\cdot$  formation is assumed. The current mechanism has no mechanistic assignments for unsaturated ketones other than MVK, and in general specific assignments would need to be given for the individual compounds.

### c. Organic Nitrate Photolysis

As discussed in Section II.A.3.b, although organic nitrate products are represented using the lumped molecule approach, the mechanism for the generic organic nitrate model species used for this purpose is derived based on generated mechanisms for individual organic nitrate compounds. The rates of



their photolysis reactions are determined as shown on Table 26, which indicates that all organic nitrates are assumed to photolyze using the absorption cross sections recommended by IUPAC (Atkinson et al, 1997a, 1999) for isopropyl nitrate. As discussed there, the quantum yield for NO<sub>2</sub> formation is assumed to be unity. In view of this, all organic nitrate photolysis reactions are represented by the general mechanism

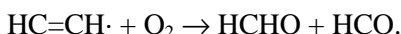


The subsequent reactions of the alkoxy radicals are then derived using the general methods discussed in Section II.B.10.

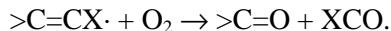
## 8. Reactions of Carbon Centered Radicals

Carbon-centered radicals are any radicals containing the groups CH<sub>3</sub>·, -CH<sub>2</sub>·, -CH[·]-, >C[·]-, HCO·, -CO·, =CH·, or =C[·]. Except as indicated below or in Table 27, these are assumed to react exclusively by O<sub>2</sub> addition, forming the corresponding peroxy group. The general exceptions are as follows:

- Vinyl radicals are assumed to react via the mechanism

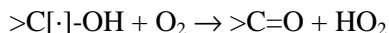


based on the data of Slagle et al (1984). Except as indicated below, substituted vinyl radicals are assumed to react analogously, e.g.,



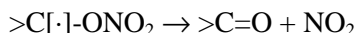
Where -X is -H or any non-radical group. The exceptions are radicals of the type HO-C=C· formed in the reactions of OH with acetylenes, where specific mechanistic assignments are made as indicated below in Table 27.

- α-Hydroxy alkyl radicals are assumed to react by O<sub>2</sub> abstraction from the -OH, forming HO<sub>2</sub> and the corresponding carbonyl compound, e.g.,



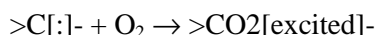
The assumption that this reaction dominates for α-hydroxy radicals is based on results of product studies of reactions of alcohols and other OH-substituted compounds in the presence of O<sub>2</sub>.

- α-Nitroxy alkyl radicals, which can be formed in the reactions of NO<sub>3</sub> radicals with alkenes, are assumed to undergo rapid unimolecular decomposition to NO<sub>2</sub> and the corresponding carbonyl compound, e.g.,



This is assumed to be an extremely rapid decomposition based on its high estimated exothermicity, combined with the expectation that the decomposition should not have a large activation energy. However, experimental (and theoretical) verification of this assumption would be useful.

- Carbenes are assumed to react with O<sub>2</sub>, forming an excited Crigee biradical, e.g.,



Although the excitation energy is almost certainly different than those formed in O<sub>3</sub> + alkene reactions, for lack of available information otherwise the excited Crigee biradicals are assumed to react with the same mechanism, and are therefore represented by the same species in the

mechanism generation system. The reactions of Crigee biradicals are discussed in Section II.B.11.

In addition to the above general exceptions, specific mechanistic assignments are made for some of the unsaturated carbon-centered radicals formed in the reactions of the special reactants that are currently supported by the system. These assignments are indicated on Table 27, along with footnotes documenting the reasons for the assignments. As shown there, there are three types of radicals that are considered, as follows:

- 1) OH-substituted vinylic radicals formed by OH addition to acetylenes whose mechanisms are assigned based on the assumed mechanism for acetylene (Carter et al, 1997c);
- 2) various allylic radicals where  $O_2$  can add at more than one radical center, where the branching ratio assignments are based primarily on data from isoprene product studies (Carter and Atkinson, 1996); and
- 3) precursors to allylic radicals that are assumed to react with  $O_2$  by abstraction forming  $HO_2$  and allylic radicals, in order to account for the formation of 3-methyl furan from the reactions of OH with isoprene (Carter and Atkinson, 1996).

Note that the assignments for the allylic radicals that are based on product data are not always consistent with each other [e.g., addition of  $O_2$  to the least substituted position is assumed for the nitrate-substituted radicals, while the opposite assumption is made for  $HO-CH_2-C(CH_2)=CH(CH_2-OH)$  to be consistent with product data]. Thus, these must be considered to be highly uncertain.

Although one might expect radicals of the type  $R-O-C(O)\cdot$  to rapidly decompose to  $R\cdot + CO_2$ , model simulations of reactivity experiments with methyl isobutyrate, which is predicted to form  $CH_3OC(O)\cdot$  radicals in high yields, cannot fit the data if this is assumed (Carter et al, 1999a). Therefore, we assume that these radicals do not decompose, but instead add  $O_2$  to form radicals of the type  $ROC(O)OO\cdot$ , which can react with  $NO_2$  to form PAN analogues of the type  $ROC(O)OONO_2$ . However, direct product data for systems where these radicals may be formed are needed to verify if this is indeed the case.

Table 27. Mechanistic assignments for carbon-centered radicals that are assumed not to react as estimated for general carbon-centered radicals.

Reactant	Product(s)	Yield	Notes
<u>OH-Substituted Vinylic Radicals (from OH + Acetylenes)</u>			
HO-CH=CH.	HCO-OH + HCO.	33%	1
	HCO-CHO + OH	67%	
CH3-C[.] =CH(OH)	HCO-OH + CH3-CO.	33%	2
	CH3-CO-CHO + OH	67%	
CH3-C[.] =CH-OH	HCO-OH + CH3-CO.	33%	2
	CH3-CO-CHO + OH	67%	
CH3-C(OH)=C[.] -CH3	CH3-CO-OH + CH3-CO.	33%	2
	CH3-CO-CO-CH3 + OH	67%	
CH3-CH2-C[.] =CH-OH	HCO-OH + CH3-CH2-CO.	33%	2
	CH3-CH2-CO-CHO + OH	67%	
<u>Allylic Radicals</u>			
CH2=CH-C[.](CH3)-CH2-OH	CH2=CH-C[OO.](CH3)-CH2-OH	67%	3,4
	HO-CH2-C(CH3)=CH-CH2OO.	16.5%	
	HO-CH2-C(CH3)=CH(CH2OO.)	16.5%	
CH2=C(CH3)-CH[.] -CH2-OH	CH2=C(CH3)-CH[OO.]-CH2-OH	59.2%	3,5
	CH3-C(CH2OO.)=CH(CH2-OH)	20.4%	
	CH3-C(CH2OO.)=CH-CH2-OH	20.4%	
HO-CH2-C(CH2.)=CH(CH2-OH)	CH2=C(CH2-OH)-CH[OO.]-CH2-OH	100%	3,6
*C(CH3)=CH-O-CH2-CH[.]-*	*O-CH=C(CH3)-CH=CH-* + HO2.	100%	3,7
*C[.](CH3)-CH=CH-O-CH2-*	*O-CH=C(CH3)-CH=CH-* + HO2.	100%	3,7
CH2=CH-C[.](CH3)-CH2-ONO2	.OOCH2-CH=C(CH3)-CH2-ONO2	100%	3,8
CH2=CH-CH[.] -CH2-OH	CH2=CH-CH[OO.]-CH2-OH	50%	9
	HO-CH2-CH=CH-CH2OO.	25%	
	HO-CH2-CH=CH(CH2OO.)	25%	
CH2=CH-CH[.] -CH2-ONO2	.OOCH2-CH=CH-CH2-ONO2	50%	3,10
	.OOCH2-CH=CH(CH2-ONO2)	50%	

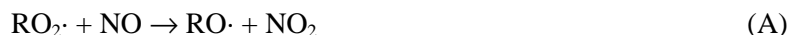
Table 27 (continued)

Reactant	Product(s)	Yield	Notes
<u>Allylic Radical Precursors</u>			
*C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-CH <sub>2</sub> -CH[.]-*	H <sub>2</sub> O + *C(CH <sub>3</sub> )=CH-O-CH <sub>2</sub> -CH[.]-*	100%	3,7
*CH(OH)-C[.](CH <sub>3</sub> )-CH <sub>2</sub> -O-CH <sub>2</sub> -*	H <sub>2</sub> O + *C[.](CH <sub>3</sub> )-CH=CH-O-CH <sub>2</sub> -*	100%	3,7
<ol style="list-style-type: none"> <li>1 Estimated mechanism is based on the data of Hatakeyama et al (1986) and modeling acetylene environmental chamber runs Carter et al (1997c).</li> <li>2 Estimated by analogy with assumed reactions of HO-CH=CH. from acetylene.</li> <li>3 Ratios of reaction of O<sub>2</sub> at different positions of the allylic radical is assumed to be as discussed by Carter and Atkinson (1996).</li> <li>4 The relative importance of this reaction is based on observed yields of methyl vinyl ketone in the reactions of OH radicals with isoprene.</li> <li>5 The relative importance of this reaction is based on observed yields of methyl vinyl ketone in the reactions of OH radicals with methacrolein.</li> <li>6 This reaction is assumed to dominate to be consistent with results of API-MS isoprene + OH product studies of Kwok et al (1995), which indicate that C<sub>5</sub>-dihydroxycarbonyls, the predicted products of the competing reactions, are not formed.</li> <li>7 It is necessary to assume this radical reacts as shown in order to explain the observed formation of 3-methyl furan from the reaction of OH radicals with isoprene (Carter and Atkinson, 1996).</li> <li>8 Assumed to dominate over addition at the least substituted end of the allylic radical to be consistent with product data, as discussed by Carter and Atkinson (1996). Formation of only one of the two possible cis-trans isomers is shown because the reactions of the other isomer are expected to give the same products.</li> <li>9 Equal probability of addition at either radical center of the allylic radical is assumed.</li> <li>10 100% terminal addition to allylic radical is assumed, to be consistent with mechanism assumed for isoprene (Carter and Atkinson, 1996). Equal probability of cis and trans formation is assumed.</li> </ol>			

## 9. Reactions of Peroxy Radicals

Peroxy radicals are critical intermediates in almost all the generated mechanisms. Although under atmospheric conditions they can react with NO<sub>2</sub>, NO<sub>3</sub>, HO<sub>2</sub>, and other peroxy radicals, the current version of the system only generates their reactions with NO. This is because reaction with NO is the major fate of peroxy radicals under conditions where reactions of VOCs contribute to tropospheric ozone, and the current base mechanism uses condensed approaches to represent the effects of the other reactions (see Section A.2.d). The reactions of non-acyl peroxy radicals with NO<sub>2</sub> are ignored because they are assumed to be rapidly reversed by the thermal decomposition of the peroxyxynitrate formed. The reactions of acyl peroxy radicals with NO<sub>2</sub> are not considered because acyl peroxy radicals are represented by lumped species so their reactions do not need to be generated. The products of peroxy + NO<sub>3</sub> and peroxy + peroxy reactions are represented by lumped species, so they are not considered in the mechanism generation system.

The main factor that needs to be determined when generating reactions of peroxy radicals with NO is the branching ratio between formation of NO<sub>2</sub> and the corresponding alkoxy radical, or addition and rearrangement forming the organic nitrate, e.g.



The rate constant ratio  $k_N/(k_A+k_N)$  is referred to as the “nitrate yield” in the subsequent discussion. This is a potentially important factor affecting a VOC’s atmospheric impact because if nitrate formation (process “N”) is a radical termination process and can significantly inhibit radical levels if it is sufficiently important compared to propagation (process “A”). Unfortunately, except for secondary peroxy radicals formed from the C<sub>3</sub>-C<sub>10</sub> n-alkanes, direct information concerning nitrate yields is extremely limited, and nitrate yields have to be either estimated or (for those few cases where this is possible) adjusted to fit overall reactivity observed in environmental chamber experiments.

For the peroxy radicals formed from alkane photooxidations, the previous version of the mechanisms used yields estimated by Carter and Atkinson (1989). These are based on data for nitrate yields from reactions of OH with C<sub>3</sub>-C<sub>8</sub> n-alkanes and several C<sub>5</sub> and C<sub>6</sub> branched alkanes at ambient temperature and pressure, and on nitrate yields at different temperatures and pressures in OH reactions of several C<sub>5</sub> and C<sub>7</sub> alkanes. The data indicate that nitrate yields from alkyl peroxy radicals increase with the size of the molecule from less than 5% for C<sub>3</sub> to ~33% for C<sub>8</sub> (with an apparent upper limit of 40-50% for larger molecules), and also increase with decreasing temperature and decrease with decreasing pressure. This suggests that the rate of the nitrate formation reaction is governed by similar factors affecting other three-body reactions, whose temperature and pressure dependences can be parameterized using a modified version of the “Troe” falloff expression that is currently used in the evaluations. Based on this, Carter and Atkinson (1989) used the following parameterization to fit the nitrate yield data for the secondary alkyl peroxy radicals:

$$Y_{\text{sec}}(n_C, T, M) = (k_N/k_R) / [1 + (k_N/k_R)] \quad (\text{III})$$

where  $Y_{\text{sec}}$  is the nitrate yield for secondary alkyl radicals with  $n_C$  carbons at temperature  $T$  (in °K) and total pressure  $M$  (in molecules cm<sup>-3</sup>), and the rate constant ratio  $k_N/k_R$  is derived from

$$k_N/k_R = \{R_0(T, n_C) \cdot M / [1 + R_0(T, n_C) \cdot M / R_\infty(T)]\} \cdot F^Z \quad (\text{IV})$$

where

$$R_0(T, n_C) = \alpha \cdot e^{\beta \cdot n_C} \cdot (T/300)^{-m_0}$$

$$R_\infty(T) = R_\infty^{300} \cdot (T/300)^{-m_\infty}$$

$$Z = \{1 + [\log_{10}\{R_0(T, n_C) \cdot M / R_\infty(T)\}]^2\}^{-1}$$

and  $\alpha$ ,  $\beta$ ,  $R_\infty^{300}$ ,  $m_0$ ,  $m_\infty$ , and  $F$  are empirical parameters that are optimized to fit the data. Based on the data available at the time, Carter and Atkinson (1989) derived  $\alpha = 1.94 \times 10^{-22}$  cm<sup>3</sup> molecule<sup>-1</sup>,  $\beta = 0.97$ ,  $R_\infty^{300} = 0.826$ ,  $m_0 = 0$ ,  $m_\infty = 8.1$ , and  $F = 0.411$ . The limited (and somewhat inconsistent) data for primary and tertiary peroxy radicals indicate that lower nitrate yields are formed from these radicals, and Carter and Atkinson (1989) recommended using scaling factors of  $0.4 \pm 0.05$  and  $0.3 \pm 0.15$  for secondary and tertiary peroxy radicals, respectively.

Most of the data concerning the effects of nitrate yields on carbon number come from the measurements of Atkinson et al (1982b, 1984), and the temperature and pressure effects data come from Atkinson et al (1983b). More recently, using what Atkinson (private communication, 1999) believes is

improved chromatographic methods, Arey et al (1999) remeasured the nitrate yields from the C<sub>3</sub>-C<sub>8</sub> n-alkanes. They obtained significantly lower nitrate yields for the C<sub>5+</sub> radicals, and Atkinson and co-workers (unpublished results, 1999) obtained nitrate yield data from n-decane than estimated using the parameterization of Carter and Atkinson (1989). For example, the new data indicate a nitrate yield of 24% for the C<sub>8</sub> secondary peroxy radicals, compared to the previous measurement of ~33%. As discussed below, these lower nitrate yields resulted in model being able to fit chamber data without having to make the chemically unreasonable assumption that hydroxy-substituted C<sub>6+</sub> peroxy radicals formed after alkoxy radical isomerizations did not form nitrates when they reacted with NO, as had to be made in previous versions of the mechanism (Carter, 1990; Carter and Atkinson, 1985). Therefore, the earlier nitrate yields of Atkinson et al (1982b, 1983b, 1984), which are all based on similar analytical methods, appear to be low.

Because of this, the parameter values of Carter and Atkinson (1989) are no longer appropriate for general estimation purposes and need to be re-derived to be consistent with the new data. To determine temperature and pressure effects, we assume that the data of Atkinson et al (1983b) are valid in a relative sense (i.e., the errors are in the nitrate calibrations), so relative changes with temperature and pressure are still correct), and correct all the data to be consistent with the remeasured yields at atmospheric temperature and pressure. Table 28 gives the nitrate yield data that were used to re-derive the parameterization, along with footnotes giving the source of the data or how they were derived. These include all the new data currently available from Atkinson's laboratory, together with the pentyl and heptyl nitrate yields at varying temperatures and pressures from Atkinson et al (1983b), corrected to be consistent with the new data. The temperature and pressure effects data for the branched secondary alkyl nitrate data from Atkinson et al (1983b) (see also Carter and Atkinson, 1989) were not used because there are no more recent data available to correct the yields, and because the pentyl and heptyl nitrate data should be a sufficient basis for the optimization.

Table 28. Alkyl nitrate yield data from the reactions of NO with secondary alkyl radicals that were used to derive the parameters to estimate secondary alkyl nitrate yields as a function of temperature, pressure, and carbon number.

Compound or Radical	nC	T (K)	P (molec cm <sup>3</sup> )	Yield				Fit	
				Uncor	Corr	Ref	Calc	Wt	Err
Propane	3	300	2.37e+19		4.0%	1,2	5.0%	100%	11%
n-Butane	4	300	2.37e+19		8.3%	1,2	7.9%	100%	-4%
n-Pentane	5	300	2.37e+19	13.4%	11.5%	1,2	11.4%	100%	0%
n-Hexane	6	300	2.37e+19		15.0%	1,2	15.3%	100%	2%
n-Heptane	7	300	2.37e+19	29.1%	18.7%	1,2	18.9%	100%	1%
n-Octane	8	300	2.37e+19		23.6%	1,2	21.8%	100%	-7%
n-Decane	10	300	2.37e+19		24.1%	2,3	25.0%	100%	4%
Cyclohexyl	6	300	2.37e+19		16.5%	4	15.3%	100%	-7%
2-Pentyl	5	284	2.52e+19	15.8%	13.5%	5	14.3%	5%	6%
	5	284	1.21e+19	10.6%	9.1%		9.7%	5%	6%
	5	284	5.27e+18	6.8%	5.8%		5.5%	5%	-3%
	5	300	1.63e+19	9.9%	8.5%		9.5%	5%	10%
	5	300	1.13e+19	9.5%	8.1%		7.7%	5%	-4%
	5	300	4.96e+18	6.0%	5.1%		4.5%	5%	-7%
	5	300	1.82e+18	3.1%	2.7%		2.0%	5%	-7%
	5	328	2.18e+19	8.2%	7.0%		7.8%	5%	8%
	5	326	1.19e+19	6.4%	5.5%		5.9%	5%	5%
	5	327	4.46e+18	3.9%	3.3%		3.2%	5%	-2%
3-Pentyl	5	337	2.12e+19	7.9%	6.8%		6.9%	5%	2%
	5	284	2.52e+19	17.4%	14.9%	3,4	14.3%	5%	-4%
	5	284	1.21e+19	12.0%	10.3%		9.7%	5%	-6%
	5	284	5.27e+18	7.5%	6.4%		5.5%	5%	-9%
	5	300	1.63e+19	10.7%	9.2%		9.5%	5%	3%
	5	300	1.13e+19	10.3%	8.8%		7.7%	5%	-11%
	5	300	4.96e+18	5.9%	5.0%		4.5%	5%	-6%
	5	300	1.82e+18	3.1%	2.7%		2.0%	5%	-7%
	5	328	2.18e+19	8.4%	7.2%		7.8%	5%	6%
	5	326	1.19e+19	6.6%	5.6%		5.9%	5%	3%
2-Heptyl	5	327	4.46e+18	4.4%	3.8%		3.2%	5%	-6%
	5	337	2.12e+19	8.1%	6.9%		6.9%	5%	0%
	7	284	2.52e+19	29.8%	19.1%		23.9%	2.5%	25%
	7	285	1.18e+19	24.9%	16.0%		18.6%	2.5%	16%
	7	283	5.43e+18	16.3%	10.5%		13.6%	2.5%	30%
	7	284	1.97e+18	11.5%	7.4%		7.4%	2.5%	1%
	7	300	1.14e+19	23.1%	14.8%		15.1%	2.5%	2%
	7	300	5.15e+18	14.6%	9.4%		10.8%	2.5%	14%
	7	300	1.80e+18	10.1%	6.5%		5.9%	2.5%	-6%

Table 28 (continued)

Compound or Radical	nC	T (K)	P (molec cm <sup>3</sup> )	Yield				Fit	
				Uncor	Corr	Ref	Calc	Wt	Err
2-Heptyl (cont'd)	7	323	2.21e+19	20.4%	13.1%		13.5%	2.5%	3%
	7	323	1.06e+19	16.3%	10.5%		10.9%	2.5%	4%
	7	324	4.65e+18	10.4%	6.7%		7.7%	2.5%	10%
	7	321	1.79e+18	7.1%	4.6%		4.7%	2.5%	2%
	7	339	2.11e+19	15.9%	10.2%		10.7%	2.5%	5%
	7	342	4.52e+18	8.9%	5.7%		6.1%	2.5%	4%
3-Heptyl	7	284	2.52e+19	35.2%	22.6%		23.9%	2.5%	6%
	7	285	1.18e+19	29.1%	18.7%		18.6%	2.5%	-1%
	7	283	5.43e+18	19.6%	12.6%		13.6%	2.5%	8%
	7	284	1.97e+18	14.1%	9.1%		7.4%	2.5%	-16%
	7	300	1.14e+19	29.3%	18.8%		15.1%	2.5%	-20%
	7	300	5.15e+18	17.7%	11.4%		10.8%	2.5%	-5%
	7	300	1.80e+18	12.2%	7.8%		5.9%	2.5%	-19%
	7	323	2.21e+19	22.6%	14.5%		13.5%	2.5%	-7%
	7	323	1.06e+19	17.9%	11.5%		10.9%	2.5%	-5%
	7	324	4.65e+18	12.2%	7.8%		7.7%	2.5%	-1%
	7	321	1.79e+18	8.8%	5.7%		4.7%	2.5%	-9%
	7	339	2.11e+19	17.2%	11.1%		10.7%	2.5%	-3%
	7	342	4.52e+18	9.6%	6.2%		6.1%	2.5%	0%
3-Heptyl	7	284	2.52e+19	31.4%	20.2%		23.9%	2.5%	18%
	7	285	1.18e+19	26.5%	17.0%		18.6%	2.5%	9%
	7	283	5.43e+18	17.6%	11.3%		13.6%	2.5%	20%
	7	284	1.97e+18	12.1%	7.8%		7.4%	2.5%	-3%
	7	300	1.14e+19	23.6%	15.2%		15.1%	2.5%	0%
	7	300	5.15e+18	15.3%	9.8%		10.8%	2.5%	10%
	7	300	1.80e+18	10.5%	6.7%		5.9%	2.5%	-8%
	7	323	2.21e+19	20.0%	12.9%		13.5%	2.5%	5%
	7	323	1.06e+19	16.0%	10.3%		10.9%	2.5%	6%
	7	324	4.65e+18	10.2%	6.6%		7.7%	2.5%	11%
	7	321	1.79e+18	7.3%	4.7%		4.7%	2.5%	0%
	7	339	2.11e+19	15.3%	9.8%		10.7%	2.5%	9%
	7	342	4.52e+18	8.4%	5.4%		6.1%	2.5%	7%

## References

- 1 Nitrate yields for secondary radicals derived from total secondary nitrate yield from reactions of the n-alkane, divided by the fraction of formation of secondary radicals, as estimated using the method of Kwok and Atkinson (1995).
- 2 Total secondary nitrate yields from Arey et al (1999).
- 3 Total secondary nitrate yield from Atkinson (unpublished data, 1999).
- 4 Aschmann et al. (1997).
- 5 Nitrate yields relative to nitrate yields at ~300K and 1 atm total pressure from Atkinson et al (1983), as tabulated by Carter and Atkinson (1989). Data placed on an absolute basis using the ~300K, 1 atm total secondary nitrate yield data from Arey et al (1999), divided by the fraction of formation of secondary radicals as estimated by the method of Kwok and Atkinson (1995).



The new parameter values were derived using a non-linear optimization procedure to minimize the sum of squares of the quantity (estimated nitrate yield - measured nitrate yield) / max (0.1, observed nitrate yield). This was used because minimizing absolute errors resulted in giving undue weight to the (somewhat uncertain) data obtained at the lowest temperature causing the derivation of unreasonable optimized parameters. On the other hand, minimizing simply relative errors put undue weight on the lowest nitrate yields, which have the highest experimental uncertainty and are least important in affecting reactivity predictions. The parameter obtained in the optimization were as follows:

$$\begin{aligned}\alpha &= 3.94 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \\ \beta &= 0.705 \\ R_{\infty}^{300} &= 0.380 \\ m_0 &= 2.15 \\ m_{\infty} &= 6.36 \\ F &= 0.745\end{aligned}$$

Note that the above value of  $R_{\infty}^{300}$ , which is essentially the upper limit nitrate yield for high molecular weight compounds at ambient temperatures, is a factor of 1.6 lower than the upper limit derived from the previous parameterization. On the other hand, nitrate yield predictions for lower molecular weight compounds under ambient conditions are not as significantly affected.

Table 28 shows the nitrate yields estimated using these reoptimized parameters. These are used as the basis for the secondary nitrate yields estimates in the current mechanism, except as indicated below. A comparison for the experimental and calculated values for these data is also shown on Figure 4. It can be seen that reasonably good fits are obtained, though there may be a slight tendency for the parameterization to underpredict the yields at the lowest temperature and highest pressure.

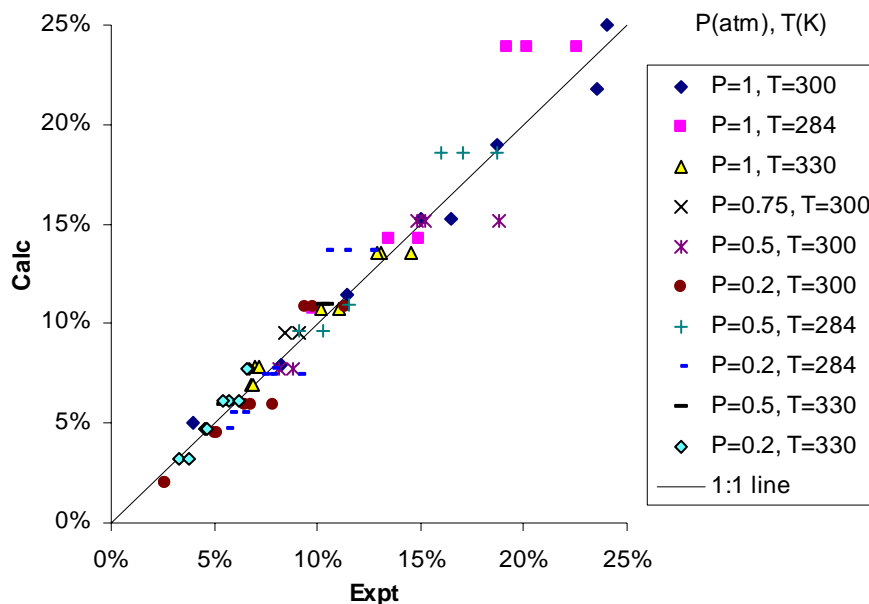


Figure 4. Plots of experimental vs calculated secondary alkyl nitrate yields that were used to optimize the parameters for estimation purposes.

The data summarized by Carter and Atkinson (1989) indicate that the parameterization that fits the data for secondary alkyl nitrates does not perform well in predicting the limited nitrate yield data for primary and tertiary peroxy radicals. In addition, the presence of -OH, -O-, -CO-, ester, or other groups may also affect nitrate yields. Available information concerning nitrate yields that can serve as a basis for deriving estimates for substituted and non-secondary peroxy radicals is given in Table 29. As indicated on the table, most of these “nitrate yields” are not results of direct measurements, but results of optimizations of nitrate yield parameters in order to fit environmental chamber data. Although these chamber data are highly sensitive to this parameter, this is obviously a highly uncertain “measurement” because the results can be affected by other uncertainties in the VOCs’ mechanisms, as well in the ability of the model to simulate the conditions of the experiment (see Section ??). Nevertheless, for most types of radicals this provides the only information available from which general estimates can be derived.

Table 29. Alkyl nitrate yield assignments used in the current mechanism, including data used to derive general estimation methods for primary, tertiary, and substituted peroxy radicals.

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated		
		Y <sub>sec</sub>	Y <sub>corr</sub>	
<u>Propane</u>				
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> OO.	2.0%	5.0%	0.0%	1
CH <sub>3</sub> -CH[OO.]-CH <sub>3</sub>	4.0%	5.0%	5.0%	2
<u>Neopentane</u>				
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> OO.)-CH <sub>3</sub>	5.1%	11.4%	6.4%	1
<u>2,2,4-Trimethyl Pentane [b]</u>				
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-CH <sub>2</sub> -C[OO.](CH <sub>3</sub> )-CH <sub>3</sub>	10.2%	21.8%	17.2%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> OO.)-CH <sub>2</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>3</sub>	10.2%	21.8%	17.2%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-CH[OO.]-CH(CH <sub>3</sub> )-CH <sub>3</sub>	12.9%	21.8%	21.9%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> OO.)-CH <sub>2</sub> -CH(CH <sub>3</sub> )-CH <sub>3</sub>	10.2%	21.8%	17.2%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-CH <sub>2</sub> -CH(CH <sub>2</sub> OO.)-CH <sub>3</sub>	10.2%	21.8%	17.2%	3
CH <sub>3</sub> -C[OO.](CH <sub>3</sub> )-CH <sub>2</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-CH <sub>2</sub> -OH	10.2%	21.8%	17.2%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> OO.)-CH <sub>2</sub> -OH	10.2%	21.8%	17.2%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -C[OO.](CH <sub>3</sub> )-CH <sub>3</sub>	7.9%	19.0%	13.4%	3
CH <sub>3</sub> -C(OH)(CH <sub>2</sub> OO.)-CH <sub>2</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>3</sub>	7.9%	19.0%	13.4%	3
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -C[OO.](CH <sub>3</sub> )-CH <sub>3</sub>	7.9%	19.0%	13.4%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-CH <sub>2</sub> -CH[OO.]-CH <sub>3</sub>	11.2%	19.0%	19.0%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> OO.)-CH <sub>2</sub> -CH(OH)-CH <sub>3</sub>	7.9%	19.0%	13.4%	3
CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -CH(CH <sub>2</sub> OO.)-CH <sub>3</sub>	7.9%	19.0%	13.4%	3
<u>2-Methyl Butane</u>				
CH <sub>3</sub> -C[OO.](CH <sub>3</sub> )-CH <sub>2</sub> -CH <sub>3</sub>	5.2%	11.4%	6.4%	1
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH[OO.]-CH <sub>3</sub> [a]	14.1%	11.4%	11.4%	1
<u>Propene</u>				
CH <sub>3</sub> -CH[OO.]-CH <sub>2</sub> -OH	1.5%	5.0%	0.0%	4
CH <sub>3</sub> -CH(CH <sub>2</sub> OO.)-OH	1.8%	5.0%	0.0%	4
<u>1-Butene</u>				
CH <sub>3</sub> -CH <sub>2</sub> -CH(CH <sub>2</sub> OO.)-OH	3.1%	7.9%	3.9%	5
CH <sub>3</sub> -CH <sub>2</sub> -CH[OO.]-CH <sub>2</sub> -OH	2.2%	7.9%	3.9%	5
<u>1-Hexene</u>				
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(CH <sub>2</sub> OO.)-OH	6.6%	15.3%	9.6%	6
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[OO.]-CH <sub>2</sub> -OH	4.9%	15.3%	9.6%	6
<u>Cis-2-Butene</u>				
CH <sub>3</sub> -CH(OH)-CH[OO.]-CH <sub>3</sub>	3.5%	7.9%	3.9%	7

Table 29 (continued)

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated		
		Y <sub>sec</sub>	Y <sub>corr</sub>	
<u>Isoprene</u>				
HO-CH <sub>2</sub> -C(CH <sub>3</sub> )=CH-CH <sub>2</sub> OO.	8.8%	11.4%	6.4%	8
HO-CH <sub>2</sub> -C(CH <sub>3</sub> )=CH(CH <sub>2</sub> OO.)	8.8%	11.4%	6.4%	8
CH <sub>2</sub> =CH-C[OO.](CH <sub>3</sub> )-CH <sub>2</sub> -OH	8.8%	11.4%	6.4%	8
CH <sub>3</sub> -C(CH <sub>2</sub> OO.)=CH(CH <sub>2</sub> -OH)	8.8%	11.4%	6.4%	8
CH <sub>3</sub> -C(CH <sub>2</sub> OO.)=CH-CH <sub>2</sub> -OH	8.8%	11.4%	6.4%	8
CH <sub>2</sub> =C(CH <sub>3</sub> )-CH[OO.]-CH <sub>2</sub> -OH	8.8%	11.4%	6.4%	8
CH <sub>2</sub> =CH-C(OH)(CH <sub>2</sub> OO.)-CH <sub>3</sub>	8.8%	11.4%	6.4%	8
CH <sub>2</sub> =C(CH <sub>3</sub> )-CH(CH <sub>2</sub> OO.)-OH	8.8%	11.4%	6.4%	8
<u>T-Butyl Alcohol</u>				
CH <sub>3</sub> -C(OH)(CH <sub>2</sub> OO.)-CH <sub>3</sub>	7.0%	7.9%	3.9%	9
<u>MTBE</u>				
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH <sub>2</sub> OO.	7.0%	11.4%	6.4%	10
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> OO.)-O-CH <sub>3</sub>	7.0%	11.4%	6.4%	10
<u>Ethoxy Ethanol</u>				
CH <sub>3</sub> -CH[OO.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	2.5%	7.9%	3.9%	11
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[OO.]-CH <sub>2</sub> -OH	2.5%	7.9%	3.9%	11
HO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> OO.	2.5%	7.9%	3.9%	11
<u>Carbitol</u>				
HO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> OO.	12.2%	15.3%	9.6%	12
CH <sub>3</sub> -CH[OO.]-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -OH	12.2%	15.3%	9.6%	12
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[OO.]-CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -OH	12.2%	15.3%	9.6%	12
CH <sub>3</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH[OO.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	12.2%	15.3%	9.6%	12
CH <sub>3</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[OO.]-CH <sub>2</sub> -OH	12.2%	15.3%	9.6%	12
<u>Methyl Acetate</u>				
CH <sub>3</sub> -CO-O-CH <sub>2</sub> OO.	1.5%	5.0%	0.0%	13
<u>2-Butoxyethanol</u>				
HO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> OO.	11.8%	15.3%	9.6%	14
CH <sub>3</sub> -CH[OO.]-CH <sub>2</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -OH	11.8%	15.3%	9.6%	14
CH <sub>3</sub> -CH <sub>2</sub> -CH[OO.]-CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>2</sub> -OH	11.8%	15.3%	9.6%	14
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[OO.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	11.8%	15.3%	9.6%	14
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[OO.]-CH <sub>2</sub> -OH	11.8%	15.3%	9.6%	14

Table 29 (continued)

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated		
		Y <sub>sec</sub>	Y <sub>corr</sub>	
<u>Ethyl Acetate</u>				
CH3-CO-O-CH2-CH2OO.	4.0%	7.9%	3.9%	15
CH3-CO-O-CH[OO.]-CH3	4.0%	7.9%	3.9%	15
CH3-CH2-O-CO-CH2OO.	4.0%	7.9%	3.9%	15
<u>Dimethyl Succinate (DBE-4)</u>				
CH3-O-CO-CH2-CH2-CO-O-CH2OO.	8.0%	15.3%	9.6%	16
CH3-O-CO-CH2-CH[OO.]-CO-O-CH3	8.0%	15.3%	9.6%	16
CH3-O-CO-CH2-CH(OH)-CO-O-CH2OO.	8.0%	15.3%	9.6%	16
<u>Dimethyl Gluturate (DBE-5)</u>				
CH3-O-CO-CH2-CH2-CH2-CO-O-CH2OO.	14.8%	19.0%	13.4%	17
CH3-O-CO-CH2-CH2-CH[OO.]-CO-O-CH3	14.8%	19.0%	13.4%	17
CH3-O-CO-CH2-CH[OO.]-CH2-CO-O-CH3	14.8%	19.0%	13.4%	17
CH3-O-CO-CH2-CH2-CH(OH)-CO-O-CH2OO.	14.8%	19.0%	13.4%	17
<u>Methyl Isobutyrate</u>				
CH3-CH(CH2OO.)-CO-O-CH3	6.4%	11.4%	6.4%	18
CH3-C[OO.](CH3)-CO-O-CH3	6.4%	11.4%	6.4%	18
CH3-CH(CH3)-CO-O-CH2OO.	6.4%	11.4%	6.4%	18
<u>t-Butyl Acetate</u>				
CH3-C(CH3)(CH2OO.)-O-CO-CH3	12.0%	15.3%	9.6%	19
CH3-C(CH3)(CH3)-O-CO-CH2OO.	12.0%	15.3%	9.6%	19
<u>Propylene Carbonate [b]</u>				
*CH(CH3)-O-CO-O-CH[OO.]-*	1.2%	7.9%	3.9%	20
*C[OO.](CH3)-CH2-O-CO-O-*	1.2%	7.9%	3.9%	20
*CH(CH2OO.)-CH2-O-CO-O-*	1.2%	7.9%	3.9%	20
CH3-CO-O-CO-O-CH2OO.	1.2%	7.9%	3.9%	20
CH3-CH[OO.]-O-CO-O-CHO	1.2%	7.9%	3.9%	20
<u>Isobutene</u>				
CH3-C[OO.](CH3)-CH2-OH	10.0%	7.9%	3.9%	21
<u>n-Butyl Acetate</u>				
CH3-CO-O-CH2-CH2-CH2-CH2OO.	10.0%	15.3%	9.6%	22
CH3-CO-O-CH2-CH2-CH[OO.]-CH3	10.0%	15.3%	9.6%	22
CH3-CH2-CH[OO.]-CH2-O-CO-CH3	10.0%	15.3%	9.6%	22
CH3-CH2-CH2-CH[OO.]-O-CO-CH3	10.0%	15.3%	9.6%	22
CH3-CH2-CH2-CH2-O-CO-CH2OO.	10.0%	15.3%	9.6%	22

Table 29 (continued)

Compound and Radical	Nitrate Yield			Ref.
	Value Used	Estimated		
		Y <sub>sec</sub>	Y <sub>corr</sub>	
<u>Cyclohexanone</u>				
*CH2-CH2-CH2-CH2-CO-CH[OO.]-*	15.0%	15.3%	9.6%	23
*CH2-CH2-CH2-CO-CH2-CH[OO.]-*	15.0%	15.3%	9.6%	23
*CH2-CH2-CO-CH2-CH2-CH[OO.]-*	15.0%	15.3%	9.6%	23
<u>1-Methoxy-2-Propanol</u>				
CH3-CH(OH)-CH[OO.]-O-CH3	1.6%	7.9%	3.9%	24
CH3-CH(OH)-CH2-O-CH2OO.	1.6%	7.9%	3.9%	24

[a] Experimental value is probably high. Not used for determining best fit parameters.

[b] Other uncertainties in the mechanism affect the nitrate yield that gives the best fits to the mechanism to such an extent that the adjusted yield for this compound was not used to determine the best fit parameters.

#### References

- 1 Based on nitrate yield data tabulated by Carter and Atkinson (1989).
- 2 Based on 2-propyl nitrate yields from propane from Arey et al (1999), corrected fraction of 2-propyl formation estimated using the method of Kwok and Atkinson (1995).
- 3 Nitrate yields from C7 and C8 peroxy radicals formed from 2,2,4-trimethyl pentane reduced by a factor of 1.7 to fit results of environmental chamber reactivity experiments.
- 4 Based on nitrate yield data from propene from Shepson et al (1985) and O'Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanovic (1976).
- 5 Based on nitrate yield data from 1-butene from O'Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanovic (1976) for propene.
- 6 Based on nitrate yield data from 1-hexene from O'Brien et al (1998), corrected for estimated fraction of reaction from terminal position based on data of Cvetanovic (1976) for propene.
- 7 Based on nitrate yield data from cis-2-butene from Muthuramu et al (1993) and O'Brien et al
- 8 Adjusted to fit environmental chamber reactivity data for isoprene (Carter and Atkinson, 1996).
- 9 Adjusted to fit environmental chamber reactivity data for t-butanol (Carter et al, 1997g).
- 10 Adjusted to fit environmental chamber reactivity data for MTBE (Carter et al, 1999a).
- 11 Adjusted to fit environmental chamber reactivity data for ethoxy ethanol (Carter et al, 1999a).
- 12 Adjusted to fit environmental chamber reactivity data for carbitol (Carter et al, 1999a).
- 13 Adjusted to fit environmental chamber reactivity data for methyl acetate (Carter et al, 1999a).
- 14 Adjusted to fit environmental chamber reactivity data for 2-butoxyethanol (Carter et al, 1999a).
- 15 Adjusted to fit environmental chamber reactivity data for ethyl acetate (Carter et al, 1999a).

Table 29 (continued)

References (continued)

- 16 Adjusted to fit environmental chamber reactivity data for DBE-4 (Carter et al, 1999a).
- 17 Adjusted to fit environmental chamber reactivity data for DBE-5 (Carter et al, 1999a).
- 18 Adjusted to fit environmental chamber reactivity data for methyl isobutyrate (Carter et al,
- 19 Adjusted to fit environmental chamber reactivity data for t-butyl acetate (Carter et al, 1999a).
- 20 Adjusted to fit environmental chamber reactivity data for propylene carbonate (Carter et al,
- 21 Adjusted to fit environmental chamber data for isobutene (Carter et al, 1999a).
- 22 Adjusted to fit environmental chamber reactivity data for n-butyl acetate (Carter et al, 1999a).
- 23 Adjusted to fit environmental chamber reactivity data for cyclohexanone (Carter et al, 1999a).
- 24 Adjusted to fit environmental chamber reactivity data for 1-Methoxy-2-Propanol (Carter et al, 1999f)

Table 29 shows that the estimates for secondary alkyl peroxy radicals (shown in the  $Y_{\text{sec}}$  column on the table) generally perform very poorly in fitting the data for these substituted or other radicals, in most cases overpredicting the observed or adjusted yields. This means that some correction is needed when estimating nitrate yields for substituted or non-secondary peroxy radicals. Carter and Atkinson (1989) recommended using a correction factor for the purpose of estimating primary and tertiary nitrate yields. This is equivalent to assuming that

$$Y_i (n_C, T, M) = Y_{\text{sec}} (n_C, T, M) \cdot f_i \quad (\text{V})$$

where  $Y_i$  is the yield computed for radicals of type  $i$ ,  $Y_{\text{sec}}$  is the yield for secondary alkyl radicals computed as shown above, and  $f_i$  is a correction factor for this type of radical. This method, if generally applied, would mean that substitution or radical structure affects nitrate yields in a way that does not depend on the size of the radical. An alternative approach is to adjust the carbon number used to estimate the yields, i.e.,

$$Y_i (n_C, T, M) = Y_{\text{sec}} (n_C - n_i, T, M) \quad (\text{VI})$$

where  $n_i$  is a correction term used to derive an “effective carbon number” for radicals of type  $i$ . This would predict that the effects of substitution or structure tend to become less important as the size of the radical increases, since the parameterization predicts that the nitrate yield becomes less dependent on  $n_C$  as  $n_C$  increases.

Figure 5 shows plots of the observed or adjusted overall nitrate yields derived for compounds forming non-secondary or substituted peroxy radicals against secondary nitrate yields ( $Y_{\text{sec}}$ ) calculated for the same number of carbons using Equations (III and IV)<sup>10</sup>. It can be seen that in most cases the ratio of the observed or adjusted yields to  $Y_{\text{sec}}$  range from ~0.4 to 1, with no apparent dependence of the ratio on the nature of the radical or its substituents. The best fit line for all the data corresponds to a correction factor of ~0.65, if the constant correction factor method (Equation V) is employed, with an uncertainty of approximately a factor of 1.6. Because of the lack of a clear dependence of the correction on the type of radical, the most appropriate approach is probably to use this factor for all substituted or non-secondary radicals.

<sup>10</sup> The adjusted nitrate yield for methyl isobutyrate, whose mechanism is highly uncertain, is not shown.

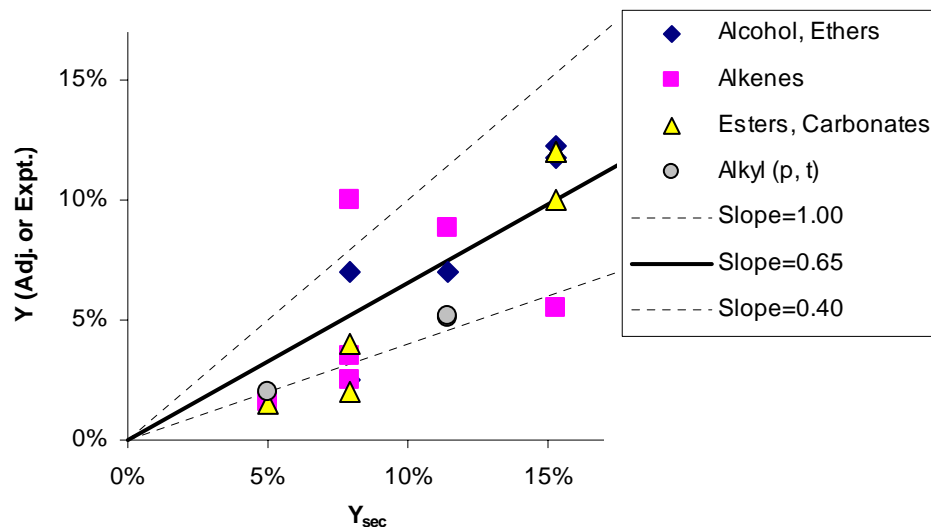


Figure 5. Plots of observed or adjusted overall nitrate yields against  $Y_{sec}$  values derived using Equations (III and IV) for compounds forming non-secondary and substituted peroxy radicals.

However, if the constant correction factor method (Equation V) is employed, then the model tends to overpredict the ozone reactivities of high molecular weight alkanes (e.g., n-octane and n-dodecane) in environmental chamber reactivity experiments (see Section ??). Better fits are obtained if higher nitrate yields from the  $C_{8+}$  OH-substituted peroxy radicals formed in the oxidations of these compounds (following 1,4-H shift isomerizations, as discussed in Section II.B.10.b) are assumed than predicted using Equation (V) and  $f=0.65$ . This suggests that the effects of substitution may decrease as the size of the radical increases, as is predicted by the “effective carbon number” adjustment approach (Equation VI). Therefore, “effective carbon number” adjustment this approach is adopted in this work.

The best fits to the available experimental or adjusted nitrate yield data for are obtained by using Equation (VI) with the carbon numbers reduced by  $\sim 1.5$  for non-secondary or substituted peroxy radicals, with no apparent dependence of the reduction on the type of radical or its substituents. Figure 6 shows the performance of this method in estimating overall nitrate yields for compounds forming substituted or non-secondary peroxy radicals that are used as the basis for deriving our estimates. The 1:1 line and lines showing a factor of 1.6 uncertainty range are also shown. A comparison of Figure 5 and Figure 6 shows that the carbon number adjustment method performs about as well (or poorly) as the factor adjustment method, with the data being an insufficient basis for choosing between them. However, the use of Equation (VI) with a carbon number reduction of 1.5 for all non-secondary or substituted radicals because of its superior performance in simulating the overall reactivities of the higher n-alkanes.



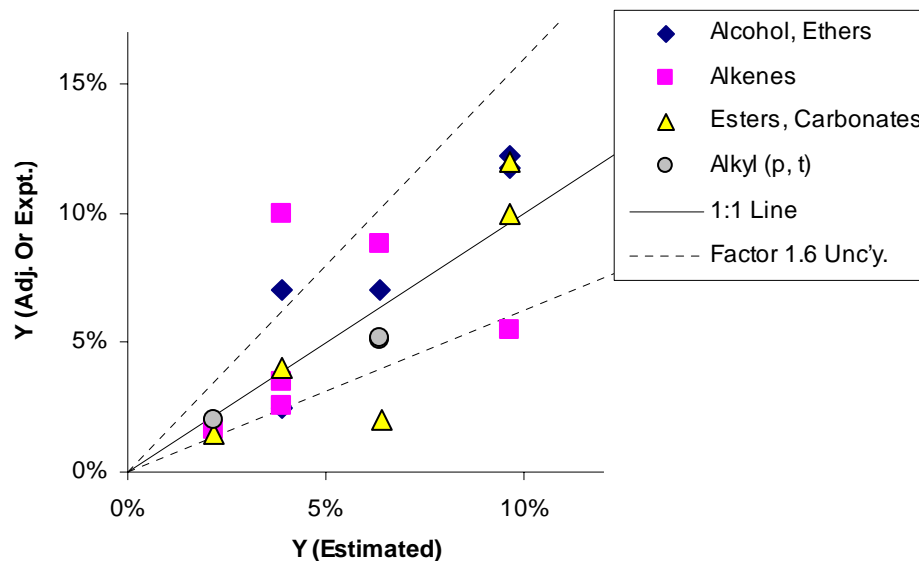


Figure 6. Plots of observed or adjusted overall nitrate yields for compounds forming non-secondary and substituted peroxy radicals against overall nitrate yields estimated using Equation (VI) and a carbon number reduction of 1.5.

There are several cases where the observed or adjusted nitrate yields are not well fit by either method. These include  $\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{OO}\cdot$  from t-butanol,  $\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CH}_2\text{OH}$  from isobutene, and  $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)(\text{CH}_3)\text{CH}_2\text{OO}\cdot$  from t-butyl acetate, where the estimated yields are considerably lower than those that must be assumed for model simulations to fit the chamber data. On the other hand, the estimates tend to underpredict nitrate yields that were measured in the reactions of OH radicals with 1-butene and 1-hexene (O'Brein et al, 1998). It is interesting to note that the cases where the nitrate yields are higher than estimated all have the radical center is at or near a quaternary carbon. However, the alkyl nitrate yield data for neopentyl, 2-methyl-2-butyl and 2-methyl-2-pentyl (Carter and Atkinson, 1989) are reasonably consistent with the predictions using the estimated corrections discussed above, so no general conclusions can be made for radicals with this structure. The reason why the nitrate yields from radicals formed from 1-butene and 1-hexene are too low is unclear, and the possibility of experimental problems cannot necessarily be ruled out.

The approach adopted in this work to use Equation (VII) with a carbon number reduction of 1.5 to derive the correction factors for estimating nitrate yields in cases of non-secondary or substituted radicals where no data are available, and to use explicit assignments for those radicals (including the outliers discussed above) for which available data indicate the estimates are not appropriate. These assignments are indicated on the “value used” column on Table 29.

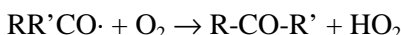
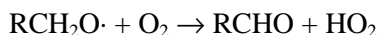
## 10. Reactions of Alkoxy Radicals

Alkoxy radicals are also critical intermediates in the photooxidation mechanisms of most VOCs, and the variety of possible reactions that higher molecular weight alkoxy radicals can undergo is a major source of the complexity (and uncertainty) in the generated photooxidation mechanisms for most VOCs. Primary and secondary alkoxy radicals can react with  $\text{O}_2$ ,  $\text{C}_{2+}$  alkoxy radicals can react via  $\beta$ -scission forming smaller molecules and radicals, long chain alkoxy radicals can undergo H-shift isomerizations

ultimately forming disubstituted radicals, and certain substituted alkoxy radicals can undergo other reactions. Knowledge of the rate constants or branching ratios for all these processes need to be specified to generate the mechanisms. Unfortunately, relevant information concerning these processes is highly limited, and estimates are usually necessary. The methods used to estimate the various rate constants or branching ratios, and the specific assignments that are used in those cases where data are available, are discussed in this section.

#### **a. Reaction with O<sub>2</sub>**

Primary and secondary alkoxy radicals can react with O<sub>2</sub>, forming HO<sub>2</sub> and the corresponding carbonyl compound.



Absolute rate constants for these reactions are available only for methoxy, ethoxy, and isopropoxy radicals, and the IUPAC recommended rate parameters (Atkinson et al, 1998) are given on Table 30. Non-Arrhenius temperature dependences are observed and the A factors are much lower than expected for an abstraction reaction, indicating a possibly complex mechanism. However, the A factors are reasonably consistent for the reactions of the different radicals, increasing as expected with the number of abstractable hydrogens, though the A factor per hydrogen for isopropoxy is approximately half that of ethoxy.

Table 30. Recommended kinetic parameters for reactions of alkoxy radicals with O<sub>2</sub>.

Radical	n	A	A/n	K(298)	ΔH <sub>r</sub>	Ea
			(cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> )		(kcal/mol)	
CH <sub>3</sub> O.	3	7.20e-14	2.40e-14	1.92e-15	-26.28	2.15
CH <sub>3</sub> -CH <sub>2</sub> O.	2	6.00e-14	3.00e-14	9.48e-15	-32.03	1.09
CH <sub>3</sub> -CH[O.]-CH <sub>3</sub>	1	1.50e-14	1.50e-14	7.67e-15	-35.82	0.40

From Atkinson (1997a), Table 9

For estimation purposes, we assume that all primary alkoxy radicals react with O<sub>2</sub> with the same A factor as does ethoxy, and that all secondary alkoxy + O<sub>2</sub> A factors are the same as for isopropoxy radicals:

$$A(\text{O}_2, \text{primary RO}\cdot) = 6.0 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$A(\text{O}_2, \text{secondary RO}\cdot) = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

Because the low A factors and non-Arrhenius behavior these estimates must be considered to be uncertain, and quantitative data are clearly needed for other alkoxy radicals.

Table 30 shows that the apparent activation energies for the alkoxy + O<sub>2</sub> reaction appear to be correlated with the heat of reaction. In fact, a plot of the activation energy vs. ΔH<sub>r</sub> (not shown) indicates that — perhaps by coincidence — the data for these three radicals fall almost exactly on a straight line, which is given by:

$$E_a(\text{O}_2) = 6.96 + 0.183 \Delta H_r(\text{O}_2) \quad (\text{VIII})$$

where E<sub>a</sub>(O<sub>2</sub>) is the activation energy and ΔH<sub>r</sub>(O<sub>2</sub>) is the heat of reaction<sup>11</sup> This therefore can be used to estimate activation energies, and therefore rate constants, for any alkoxy + O<sub>2</sub> reaction.

However, the above equation cannot be used for estimating activation energies for reactions of O<sub>2</sub> with alkoxy radicals such as CH<sub>3</sub>OCH<sub>2</sub>O·, whose reaction with O<sub>2</sub> are sufficiently exothermic that Equation (VIII) predicts a negative activation energy. In those cases, we assume for estimation purposes that no alkoxy + O<sub>2</sub> reaction has an activation energy that is less than the a certain minimum value, which should be somewhere between 0 and 0.4 kcal/mole. We assume that the actual minimum is near the high end of this range, or 0.4 kcal/mole. Therefore, for estimation purposes we use:

$$E_a(\text{O}_2) = \max [ 0.4, 6.96 + 0.183 \Delta H_r(\text{O}_2) ] \quad (\text{IX})$$

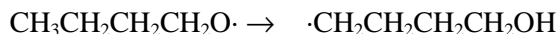
Note that the 0 to 0.4 kcal/mole range for the minimum activation energy amounts to an uncertainty in the rate constant of a factor of ~2 for highly exothermic alkoxy + O<sub>2</sub> reactions. This is not a large uncertainty given the uncertainty in assuming that the A factors for the O<sub>2</sub> reactions are the same for all primary or all secondary alkoxy radicals.

<sup>11</sup> Heats of reaction are estimated by group additivity as discussed in Section II.C.1.e, based primarily on the thermochemical groups in the NIST (1994) database. Some reactants or products had groups that are not in the NIST (1994) database, and the thermochemical contributions of these groups had to be estimated. Tabulated heats of reaction may be uncertain by at least 2 kcal/mole.

The estimates for the reactions of O<sub>2</sub> with the saturated hydrocarbon alkoxy radicals (i.e., alkoxy radicals containing only -CH<sub>3</sub>, -CH<sub>2</sub>-, >CH-, or >C< groups) are probably the least uncertain because they are the most similar to the simple alkoxy radicals used as the basis for the estimate. These estimates become increasingly uncertain for the oxygenated radicals with significantly higher reaction exothermicities (i.e., the reaction of O<sub>2</sub> with CH<sub>3</sub>OCH<sub>2</sub>O· has an estimated ΔH<sub>r</sub> of -46.6 kcal/mole, compared to -35.8 for isopropoxy). The estimates used here predict that these highly exothermic alkoxy + O<sub>2</sub> reactions have 298K rate constants of ~3 x 10<sup>-14</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> for primary radicals and ~8 x 10<sup>-15</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> for secondary radicals. However, the possibility that these rate constants may be orders of magnitude higher cannot be ruled out. For example, if the approach of Atkinson (1997a), which uses a relationship between the rate constant (not the activation energy) and the heat of reaction, estimates the rate constant for the reaction of O<sub>2</sub> with, for example, CH<sub>3</sub>OCH<sub>2</sub>O·, to be ~3.7 x 10<sup>-13</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, which is a factor of ~12 higher than the estimation approach discussed above. This, of course, would imply that the effective A factors for these highly exothermic reactions are significantly higher than for those radicals whose rate constants have been measured – which we assume is not the case.

### b. H-Shift Isomerizations

Long chain alkoxy radicals can react unimolecularly by abstraction by the alkoxy center from a C-H bond elsewhere in the radical, via a cyclic transition state, forming a hydroxy-substituted carbon-centered radical, e.g.,



Rate constants for these reactions can be estimated based on activation energies for bimolecular H-atom abstractions by alkoxy radicals plus ring strain energies for the cyclic transition states, and estimates of A factors (Carter et al, 1976; Baldwin et al, 1977; Carter and Atkinson, 1985; Atkinson, 1994). The results indicate that 1,5-H shift reactions (such as shown above), involving a relatively unstrained 6-member ring transition state, will be relatively rapid and should dominate over competing processes, at least for the hydrocarbon alkoxy radicals formed in alkane photooxidation systems. On the other hand, the estimates indicate that hydrogen shifts involving strained transition states, such as 1,3-H shifts involving a 5 member ring, as well as those involving more strained rings, are not likely to be sufficiently rapid to be important. Therefore except for the “ester rearrangement” reaction discussed below, only 1,4 H shift isomerizations are considered when the estimated mechanisms are generated.

The only data available concerning rates of 1,5-H shift isomerizations of alkoxy radicals are rate constants relative to competing alkoxy + O<sub>2</sub> or decomposition reactions. Although the rate constants for the competing reactions have also not been measured, they can be estimated in the case of the O<sub>2</sub> reactions as discussed above. Table 31 lists the isomerization reactions whose rate have been determined relative to the competing O<sub>2</sub> reaction, together with the rate constant ratios as summarized by Atkinson (1997a). Table 31 also shows the A factors estimated by Atkinson (1997a) and the corresponding activation energies, which are based on assuming

$$A(\text{isom}) = 8.0 \times 10^{10} \times (\text{number of abstractable hydrogens}) \text{ sec}^{-1}.$$

This is based on the previous estimates of Baldwin et al (1977), and is incorporated in the 1,4-H shift estimates used in this work.

Table 31. Rate constants for H abstraction reactions by alkoxy radicals.

Reaction	BDE [a] (kcal)	A [b]	Ea (kcal)	T (K)	k(T)	Refs [c]
<u>Alkoxy Isomerizations (sec<sup>-1</sup>)</u>						
1-Butoxy [d]	101.4	2.4e+11	8.42	<u>298</u>	<u>1.60e+5</u>	1,2
2-Pentoxy [d]	101.4	2.4e+11	8.16	<u>298</u>	<u>2.50e+5</u>	1,2
3-Hexoxy	101.4	2.4e+11	8.04	<u>298</u>	<u>3.05e+5</u>	2,3
2-Hexoxy	98.1	1.6e+11	6.44	<u>298</u>	<u>3.05e+6</u>	2,4
<u>Methoxy + RH Reactions (cm<sup>3</sup> molec<sup>-1</sup> sec<sup>-1</sup>)</u>						
CH <sub>4</sub>	104.9	<u>2.6e-13</u>	8.84			5
C <sub>2</sub> H <sub>6</sub> -> i-C <sub>2</sub> H <sub>5</sub>	101.2	<u>4.0e-13</u>	7.09			5
C <sub>3</sub> H <sub>8</sub> -> i-C <sub>3</sub> H <sub>7</sub>	98.6	<u>2.4e-13</u>	4.57			6
(CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> ) <sub>2</sub>	96.8	1.7e-13	4.11	<u>373</u>	<u>6.64e-16</u>	7,8
CH <sub>3</sub> OH -> CH <sub>2</sub> OH	98.1	<u>5.0e-13</u>	<u>4.07</u>			9
CH <sub>3</sub> CHO	85.9	8.4e-14	0.63	<u>298</u>	<u>2.88e-14</u>	8,10
<u>Alkoxy Isomerization Group Rate Constants for estimations (sec<sup>-1</sup>)</u>						
-CH <sub>3</sub>	101.4	2.4e+11	8.49	298	1.44e+5	2,11
-CH <sub>2</sub> -	98.1	1.6e+11	6.33	298	3.63e+6	2,11
-CH<	96.8	8.0e+10	5.51	298	7.29e+6	2,11
-CHO	85.9	8.0e+10	5.75	299	5.02e+6	2,12

[a] Bond dissociation energies are derived from the NIST (1994) thermochemical database or from heats of formation given in the IUPAC evaluation (Atkinson et al, 1997).

[b] Underlined A, Ea, T, or k data are experimental measurements. Data not underlined are estimates.

[c] Notes and references:

- 1 Rate constant recommended by Atkinson (1997a)
- 2 A factors estimated for general alkoxy radical isomerizations by Atkinson (1997a), based on earlier estimates of Baldwin et al (1977)
- 3 Use middle value of range given by Eberhard et a. (1995). Varies from 1.8 - 4.3 x 10<sup>5</sup> sec<sup>-1</sup>.
- 4 Use middle value of range given by Eberhard et a. (1995). Varies from 1.4 - 4.7 x 10<sup>6</sup> sec<sup>-1</sup>.
- 5 Tsang and Hampson (1986)
- 6 Tsang (1988)
- 7 Alcock and Mile (1975)
- 8 A factor per abstracted hydrogen is assumed to be the average of that for the methoxy + ethane, propane and propane (to isopropyl) reactions.
- 9 Tsang (1987)
- 10 Weaver et al, (1975), Kelly and Keicklen (1978). These report rate constant ratios relative to methoxy + O<sub>2</sub> of 14-15. Placed on an absolute basis using the methoxy + O<sub>2</sub> rate constant.
- 11 Activation energy derived from correlation between methoxy + RH rate constants and BDE, with an added 1.6 kcal/mole "strain" correction for consistency with data for isomerization reactions, as discussed in the text.
- 12 Activation energy estimated from that estimated for the methoxy + acetaldehyde reaction, plus the 1.6 kcal/mole "strain" correction used for the other groups, plus an additional 3.5 kcal/mole "strain" correction for reactions with -CO- groups in the transition state, derived as discussed in the text.

[d] These parameters are explicitly assigned for this radical in the mechanism generation system.

The limited number of species for which isomerization rate constants have been measured and the relative imprecision of the data for 2-hexoxy provide an inadequate data base from which to derive a general estimation method for the activation energies. It is reasonable to assume that the activation energy will be correlated with the C-H bond dissociation energy for the bond that is being attacked by the alkoxy center. To provide a somewhat larger database in this regard, it is useful to look at available kinetic information for a bimolecular analogue for this reaction, namely the H-atom abstraction reactions of methoxy radicals. Table 31 lists the rate constants or Arrhenius parameters found for such reactions in the NIST kinetics database (NIST, 1989). The Arrhenius parameters have been estimated for those species where temperature dependence information was not given by using the average of those determined for methoxy + methane and methoxy + ethane. The measured (IUPAC, 1997) or estimated (NIST, 1994) bond dissociation energies (BDE's) for the C-H bond being attacked are also shown on the Table.

Figure 7 shows plots of the activation energies for the internal or bimolecular alkoxy H-atom abstraction reactions against the relevant bond dissociation energy. [Data for the methoxy + isobutane reaction are inconsistent (NIST 1998), so they are not included.] It can be seen that if the methoxy + acetaldehyde data are not included, then a reasonably good straight line relationship is obtained. The limited data for the isomerization reactions are consistent with the relationship for the bimolecular methoxy reactions, with an offset of 1.6 kcal/mole. Although this offset is probably not outside the uncertainties of the BDE or activation energy determinations, it could also be rationalized as ring strain in the 6-member ring transition state for the isomerization reaction.

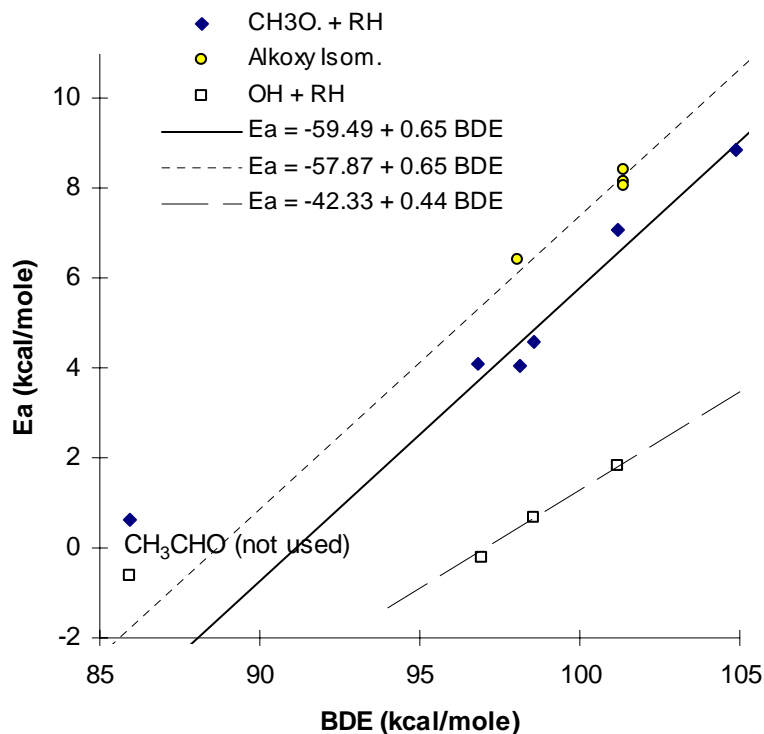


Figure 7. Plot of activation energies vs bond dissociation energies for methoxy abstraction reactions, alkoxy radical isomerizations, and OH abstraction reactions.

The solid line shown on Figure 7 is the least squares line through the data for the methoxy abstraction reactions, with the data for acetaldehyde not being used when determining the fit. The measurement for acetaldehyde is excluded because abstractions from (CO)-H bonds apparently do not have the same correlation with the bond energies as abstractions from hydrocarbon C-H bonds.

The dotted line on Figure 7 shows the line for the methoxy reaction offset by 1.6 kcal/mole to agree with the data for the isomerizations of the butoxy, pentoxy, and hexoxy radicals. Therefore, this can be used as a basis for estimating activation energies for alkoxy radical isomerizations in general, or at least those involving abstractions from alkyl C-H bonds.

The rate constants for any isomerization reaction can be estimated using a generalization of the structure-reactivity approach derived by Atkinson (Atkinson, 1987, Kwok and Atkinson, 1995, Atkinson, 1997a) for estimating OH radical reactions. In this approach, reaction by H-abstraction at each type of group, whether -CH<sub>3</sub>, -CH<sub>2</sub>-, -CH<, or -CHO is given by a group rate constant for that group, multiplied by an appropriate correction factor for each substituent other than methyl groups (whose correction factor is 1.0 by definition). Note that the substituting corrections are assumed to be due only to the substituting affecting the activation energy, not the A factor (Kwok and Atkinson, 1995; Atkinson, 1997a).

Obviously a large kinetic database is necessary to derive the substituent correction factors, and this is not available for these alkoxy radical abstraction reactions. However, if we assume that (1) the substituent corrections are due only to the substituent affecting the activation energy and not the A

factor, and (2) the activation energy is linearly related to the bond dissociation energy for both the OH and the alkoxy radical abstraction reactions, then one can derive the substituent correction factors for the alkoxy reactions from those for the corresponding OH radical reaction. The latter have been derived by Kwok and Atkinson (1996) using the large kinetic database for OH radical reactions. The first assumption is reasonable, and is already incorporated in the way the Atkinson estimation methods derive temperature dependences. The second assumption is already incorporated in our alkoxy radical estimation methods discussed above, but needs to be examined in the case of OH radical rate constants.

The 298K group rate constants used in estimating OH radical reactions and parameters used by Kwok and Atkinson (1996) to determine their temperature dependences, are given in Table 9, above. Kwok and Atkinson (1996) gave the temperature dependences in the form  $k = C T^2 \exp(-B/T)$ , but these can be recast to the Arrhenius activation energy (adjusted to be valid for T around 298K), to place it on the same basis as used for the alkoxy radical reactions listed in Table 2. The corresponding activation energies are 1.82, 0.68, -0.20, and -0.62 kcal/mole for -CH<sub>3</sub>, -CH<sub>2</sub>-, -CH<, and -CHO, respectively. These activation energies are plotted against the bond dissociation energies associated with the group on Figure 7. It can be seen that the activation energies are reasonably well fit by a linear relationship with the bond dissociation energy for reactions at alkyl C-H bonds, but not for reaction at -CHO groups. In the case of OH radicals, the correlation breaks down for bond dissociation energies less than ~95 kcal/mole because there is essentially no energy barrier for bonds weaker than that. However, for stronger bonds, the correlation between group activation energy and BDE seems to hold reasonably well.

It is of interest to note that the slope for the line relating Ea to BDE for the alkoxy reactions is somewhat greater than that for the OH reactions, by a factor of ~1.5. This means that the activation energies for the alkoxy reactions would be more sensitive to substituents than is the case for OH reactions, as might be expected given the slower rates of these reactions. If these linear relationships between Ea and BDE are assumed to hold for the substituted species, this suggests that the group correction factors for the alkoxy radical isomerizations ( $F_{\text{isom}}$ ) should be related to those for the OH radical reactions ( $F_{\text{OH}}$ ) by

$$F_{\text{isom}} \approx f_{\text{OH}}^{1.5} \quad (\text{X})$$

Thus, the group correction factors given by Kwok and Atkinson (1996) for estimating rate constants for OH radical reactions can be used as a basis for estimating alkoxy radical isomerization reactions.

The dotted line on Figure 7 was derived to fit data primarily for radicals that have a -CH<sub>2</sub>- attached to the -CH<sub>3</sub> group where the reaction is occurring. The OH group correction factor at ~300K for a -CH<sub>2</sub>- substituent is 1.23, which from Equation (X) corresponds to a correction factor of 1.5 for alkoxy radical reactions. This corresponds to an activation energy reduction of 0.18 kcal/mole. This means that the intercept for the line adjusted to fit the activation energy for these radicals (the dotted line on Figure 7) should be increased by 0.18 for the purpose of estimating group rate constants, which are defined based on -CH<sub>3</sub> substituents. Based on this, the activation energies for group rate constants for alkoxy radical isomerizations involving abstractions from -CH<sub>3</sub>, -CH<sub>2</sub>- and -CH< can be estimated from

$$E_a(\text{group isom}) = -57.87 + 0.65 \text{ BDE} + 0.18 = 57.69 + 0.65 \text{ BDE} \quad (\text{XI})$$

where BDE is the bond dissociation energy for the breaking bond. To place the BDE's on the same basis as those used to derive the equation, the BDE's for Equation (XII) should be calculated for groups with one -CH<sub>2</sub>- substituent, with the other substituents, if any, being CH<sub>3</sub> groups.

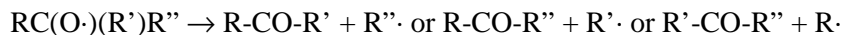
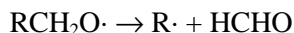


Table 31 shows the activation energies for the various alkyl groups derived using Equation (XI), along with their corresponding A factors and 298K rate constants. In the case of -CHO groups, the activation energy is estimated from the estimated methoxy + acetaldehyde activation energy, plus the estimated 1.6 kcal/mole strain energy, derived as discussed above, plus an additional 3.5 kcal/mole of strain for reactions with -CO- groups in the cyclic transition state, derived as discussed in Section II.B.10.d, below. These group rate constants, together with the substituent factors derived for Equation (XI) using the substituent factors for estimating OH radical rate constants from Table 9, above, can then be used for estimating isomerization rate constants for any alkoxy radicals where the abstraction is at the given group.

As indicated above, a comparison of the activation energies for the bimolecular methoxy reactions with the estimation activation energies for isomerization of butoxy, pentoxy and hexoxy suggests that the ring strain for these isomerizations is ~1.6 kcal/mole. Note that this is reasonably consistent with the ring strain given by Benson (1976) for a six member ring with one oxygen. However, the strain may be different if the ring in the transition state involves groups other than just -CH<sub>2</sub>-. We assume that there is no strain difference if the transition state ring also has -CH< or >C< groups, but this does not appear to be the case if the ring also contains -O-, -CO- or -O-CO- groups. In particular, predictions are more consistent with available data if activation energies for isomerization involving -O-, -CO- or -O-CO- in the transition states are increased by an additional ~3.5 kcal/mole. Before giving the basis for this, which is discussed in Section II.B.10.d, it is necessary to first discuss the rate constant estimates for the competing decomposition reactions. This is given in the following section.

### c. Beta Scission Decomposition

The most common unimolecular reactions of alkoxy radicals are  $\beta$ -scission decompositions. These involve breaking the C-C bond next to the alkoxy group, forming a carbonyl compound and a carbon center radical (where the latter will react further, as discussed above). For primary, secondary, and tertiary alkoxy radicals, the respective reactions are:



Note that for secondary and tertiary radicals there may be more than one possible reaction route, if the R, R' and/or R'' substituents are different.

No direct measurements of absolute rate constants for alkoxy radical decompositions are available, but information is available concerning ratios of these rate constants relative to those for other alkoxy radical reactions. The only information concerning temperature dependent rate constants come from the measurements relative to alkoxy + NO reactions, whose absolute rate constants are known or can be estimated (Atkinson, 1994, and references therein). Based on these data, Atkinson (1994, 1997b) recommends estimating the Arrhenius A factors using

$$A = 2.0 \times 10^{14} \cdot n \text{ sec}^{-1}, \quad (\text{XIII})$$

where n is the reaction path degeneracy. The recommended decomposition rate constants and kinetic parameters are summarized on Table 32. The A factors derived using Equation (XIII) are assumed to be applicable to all alkoxy radical decompositions. Table 32 also gives alkoxy radical decomposition rate constants obtained from rate constant ratios obtained from results of various mechanistic and product

studies, and placed on an absolute basis using estimates for the competing decomposition reactions. This is discussed below.

Table 32. Summary of measured or estimated rate constants for alkoxy radical decompositions.

Reaction	Rate Parameters [a]				Relative to			Note	Ea (est.)	
	$\Delta H_r$	A	Ea	k(298)	Type	Ratio	k(ref) [b]		Value	Err
<u>Reactions forming CH<sub>3</sub>.</u>										
CH <sub>3</sub> -CH <sub>2</sub> O. -> CH <sub>3</sub> . + HCHO	13.04	2.0e+14	<u>20.20</u>	3.1e-1	k(NO)	-		[c]	19.8	-0.4
CH <sub>3</sub> -CH[O.]·-CH <sub>3</sub> -> CH <sub>3</sub> -CHO + CH <sub>3</sub> .	7.86	4.0e+14	<u>17.60</u>	5.0e+1	k(NO)	-		[c]	17.5	-0.1
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]·-CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -CHO + CH <sub>3</sub> .	7.63	2.0e+14	<u>16.60</u>	1.3e+2	k(NO)	-		[c]	17.4	0.8
CH <sub>3</sub> -C[O.]·(CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> .	4.98	7.5e+14	<u>16.20</u>	9.9e+2	k(NO)	-		[c,d]	16.2	0.0
CH <sub>3</sub> -C[O.]·(CH <sub>3</sub> )CH <sub>2</sub> -CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> .	4.82	4.0e+14	<u>18.30</u>	1.5e+1	k(NO)	-		[c,e,f]	16.2	-2.1
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH[O.]·-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CHO	-4.81	2.0e+14	12.30	1.9e+5	k(O <sub>2</sub> )	4.85	3.9e+4	12 [f]	11.9	-0.4
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]·-CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -O-CHO + CH <sub>3</sub> .	-4.81	2.0e+14	11.49	7.5e+5	k(O <sub>2</sub> )	19	3.9e+4	10 [f]	11.9	0.4
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]·-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CHO	-4.81	2.0e+14	11.92	3.6e+5	k(O <sub>2</sub> )	9.3	3.9e+4	35 [f]	11.9	0.0
CH <sub>3</sub> -CH[O.]·-O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> CH <sub>3</sub> . + HCO-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	-4.81	2.0e+14	12.33	1.8e+5	k(O <sub>2</sub> )	4.62	3.9e+4	21 [f]	11.9	-0.4
<u>Reactions forming CH<sub>3</sub>-CH<sub>2</sub>. and CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>.</u>										
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]·-CH <sub>3</sub> -> CH <sub>3</sub> -CHO + CH <sub>3</sub> -CH <sub>2</sub> .	6.94	2.0e+14	13.58	2.2e+4	k(O <sub>2</sub> )	0.56	3.9e+4	2 [f]	14.3	0.7
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]·-CH <sub>2</sub> -CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -CHO + CH <sub>3</sub> -CH <sub>2</sub> .	6.71	4.0e+14	13.92	2.5e+4	k(O <sub>2</sub> )	0.63	3.9e+4	3 [f]	14.2	0.3
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]·-CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> . + CH <sub>3</sub> -CHO	6.13	2.0e+14	<u>14.10</u>	9.1e+3	k(NO)	-		[c]	13.9	-0.2
CH <sub>3</sub> -C[O.]·(CH <sub>3</sub> )-CH <sub>2</sub> -CH <sub>3</sub> -> CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> -CH <sub>2</sub> .	4.06	2.0e+14	<u>13.90</u>	1.3e+4	k(NO)	-		[c]	13.0	-0.9
<u>Reactions forming CH<sub>3</sub>-C[.]·(CH<sub>3</sub>)-CH<sub>3</sub></u>										
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> O.)-CH <sub>3</sub> -> HCHO + CH <sub>3</sub> -C[.]·(CH <sub>3</sub> )-CH <sub>3</sub>	10.40	2.0e+14	11.16	1.3e+6	k(O <sub>2</sub> )	39	3.4e+4	1 [f]	11.2	0.0
<u>Reactions forming alpha-Hydroxy Alkyl Radicals</u>										
HO-CH <sub>2</sub> -CH <sub>2</sub> O. -> HO-CH <sub>2</sub> . + HCHO	11.79	2.0e+14	12.61	1.1e+5	k(O <sub>2</sub> )	3.59	3.1e+4	4 [f]	12.6	0.0
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH[O.]·-CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> . + HO-CH <sub>2</sub> .	7.15	2.0e+14	11.40	8.7e+5	kd(R <sub>2</sub> CH.)	2.45	3.6e+5	7 [f]	10.6	-0.8
<u>Reactions forming CH<sub>3</sub>C(O)CH<sub>2</sub>. Radicals</u>										
CH <sub>3</sub> -CO-CH <sub>2</sub> -CH[O.]·-CH <sub>3</sub> -> CH <sub>3</sub> -CHO + CH <sub>3</sub> -CO-CH <sub>2</sub> .	3.86	2.0e+14	12.38	1.7e+5	k(O <sub>2</sub> )	4.26	3.9e+4	41 [f]	12.9	0.6
<u>Reactions forming Alkoxy Radicals</u>										
CH <sub>3</sub> -O-CH <sub>2</sub> -O-CH <sub>2</sub> O. -> CH <sub>3</sub> -O-CH <sub>2</sub> O. + HCHO	13.34	2.0e+14	13.41	2.9e+4	k(O <sub>2</sub> )	~0.19	1.6e+5	8 [f]	14.3	0.9
CH <sub>3</sub> -C[O.]·(CH <sub>3</sub> )-O-CH <sub>3</sub> -> CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> O.	9.50	2.0e+14	11.83	4.2e+5	kd(CH <sub>3</sub> .)	0.15	2.8e+6	14 [f]	12.6	0.8
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-C[O.]·(CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> -CH(CH <sub>2</sub> O.)-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	9.29	2.0e+14	11.61	6.1e+5	kd(CH <sub>3</sub> .)	0.21	2.8e+6	18 [f]	12.5	0.9
CH <sub>3</sub> -C[O.]·(CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CO-CH <sub>3</sub>	9.28	2.0e+14	11.18	1.3e+6	kd(CH <sub>3</sub> .)	0.44	2.8e+6	15 [f]	12.5	1.3
<u>Reactions forming R-CO-O. Radicals</u>										
CH <sub>3</sub> -C[O.]·(CH <sub>3</sub> )-O-CO-CH <sub>3</sub> -> CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> -CO <sub>2</sub> .	10.73	2.0e+14	16.61	1.3e+2?	kd(CH <sub>3</sub> .)	0.32	4.2e+2?	40 [f]	16.7	0.1

Table 32 (continued)

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- [a] Data from Table 33 unless noted otherwise. Rate constants and A factors in units of sec<sup>-1</sup>, and Ea;s and heats of reaction are in units of kcal/mole. Underlined Ea from references, otherwise Ea's computed from tabulated k(298) and A. These parameters are explicitly assigned for this radical in the mechanism generation system, unless indicated otherwise.
- [b] k(ref) for O<sub>2</sub> reaction is k(O<sub>2</sub>)[O<sub>2</sub>] for [O<sub>2</sub>] = 5.16 x 10<sup>18</sup> molec cm<sup>-3</sup> at 1 atm and 298K.
- [c] Atkinson (1997b). Relative to k(RO+NO) = 2.3 x 10<sup>-11</sup> exp(150/T).
- [d] High pressure limit. Batt and Robinson (1987) calculate that rate constant under atmospheric conditions is ~80% of this. However, to fit chamber data, the A factor for atmospheric modeling is increased to from 6.0 to 7.5 x 10<sup>14</sup> sec<sup>-1</sup>.
- [e] Not used when computing best fit parameters for reactions forming methyl radicals. No explicit assignments made for this radical.
- [f] Number is the radical number on Table 33 from which the data are taken. See footnotes to that table for documentation.
- [g] Not used for deriving general estimates for reactions forming this radical because of uncertainties in the rate constant ratio and the value of the reference rate constant.
- [h] The reference rate constant is almost certainly incorrect, since it would mean that the competing isomerization reaction, which isn't observed, would dominate. No explicit assignments made for this radical.

Table 33 lists the various alkoxy radicals for which relevant data are available concerning the branching ratios for their various competing reactions, or at least concerning upper or lower limits for those branching ratios. These are determined from product yields observed in various studies of OH radical + organic + NO<sub>x</sub> systems where these alkoxy radicals are expected to be formed, as indicated in the comments on the table. In some cases product yield ratios can be used to derive ratios of rate constants involving an alkoxy radical decomposition; these are indicated in Table 33 and the relevant data are also included in Table 32. (In those cases Table 32 also gives the radical number used on Table 33 to aid the reader in finding the data on that radical.) In many other cases, only upper or lower branching ratios can be derived. For example, lower limits for a reaction route can be based on observing high yields of a product expected from a reaction, and upper limits for another route can be inferred from the failure to observe an expected product from the reaction. Many of the upper or lower limit estimates are subjective and approximate, and probably in many cases they could be refined based on a detailed analysis of the experimental methods. However, these approximate upper and lower limit data are useful for assessing the overall performance of the estimation methods because of the relatively large number and variety of reactions involved.

Table 33. Experimental and estimated branching ratios for radicals where relevant data are available.

Radical Reaction	Type	$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
			k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
1 <u>CH<sub>3</sub>-C(CH<sub>3</sub>)(CH<sub>2</sub>O.)-CH<sub>3</sub></u>										
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> O.)-CH <sub>3</sub> + O <sub>2</sub> -> CH <sub>3</sub> -C(CH <sub>3</sub> )(CHO)-CH <sub>3</sub> + HO <sub>2</sub> .	O <sub>2</sub>	-30.8	3.35e+4	3%	0%	3%	5%	ok		
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> O.)-CH <sub>3</sub> -> HCHO + CH <sub>3</sub> -C[.](CH <sub>3</sub> )-CH <sub>3</sub>	D	10.4	1.31e+6	98%	75%	98%	100%	ok	<u>kd/kO<sub>2</sub></u> 39	39
Based on data summarized by Atkinson (1997b)										
2 <u>CH<sub>3</sub>-CH<sub>2</sub>-CH[O.]</u> -CH <sub>3</sub>										
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]	O <sub>2</sub>	-36.0	3.94e+4	86%	46%	64%	76%	High		
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]	D	6.9	6.46e+3	14%	24%	36%	54%	Low	<u>kd/kO<sub>2</sub></u> 0.56	0.16
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]	D	7.6	3.43e+1	0%						
Average of rate constant ratios reported by Carter et al (1979) and Cox et al (1981) as given by Atkinson (1997b).										
3 <u>CH<sub>3</sub>-CH<sub>2</sub>-CH[O.]</u> -CH <sub>2</sub> -CH <sub>3</sub>										
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]	O <sub>2</sub>	-36.3	3.94e+4	72%	42%	61%	74%	ok	<u>kd/kO<sub>2</sub></u> 0.63	0.39
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]	D	6.7	1.53e+4	28%	26%	39%	58%	ok		
Based on data of Atkinson et al (1995).										
4 <u>HO-CH<sub>2</sub>-CH<sub>2</sub>O.</u>										
HO-CH <sub>2</sub> -CH <sub>2</sub> O. + O <sub>2</sub> -> HO <sub>2</sub> . + HCO-CH <sub>2</sub> -OH	O <sub>2</sub>	-30.6	3.10e+4	22%	15%	22%	30%	ok		
HO-CH <sub>2</sub> -CH <sub>2</sub> O. -> HO-CH <sub>2</sub> . + HCHO	D	11.8	1.11e+5	78%	70%	78%	85%	ok	<u>kd/kO<sub>2</sub></u> 3.59	3.59
Based on product data for ethene, as recommended by Atkinson (1997a).										
5 <u>CH<sub>3</sub>-CH[O.]</u> -CH <sub>2</sub> -OH										
CH <sub>3</sub> -CH[O.]	O <sub>2</sub>	-34.6	2.68e+4	1%						
CH <sub>3</sub> -CH[O.]	D	6.6	5.19e+6	99%	85%	100%	100%	ok		
Based on product data for propene, as discussed by Atkinson (1997a).										
6 <u>CH<sub>3</sub>-CH(OH)-CH[O.]</u> -CH <sub>3</sub>										
CH <sub>3</sub> -CH(OH)-CH[O.]	O <sub>2</sub>	-34.8	2.91e+4	0%	0%	0%	0%	ok		
CH <sub>3</sub> -CH(OH)-CH[O.]	D	2.9	2.56e+9	100%	100%	100%	100%	ok		
CH <sub>3</sub> -CH(OH)-CH[O.]	D	9.1	1.18e+1	0%						
Based on upper limit yields of hydroxy carbonyls from OH + trans-2-butene (Atkinson, personal communication, 1999). Similar results were obtained from OH + trans-3-hexene.										

Table 33 (continued)

Radical		$\Delta H_f$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
Reaction	Type		k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
7 <u>CH<sub>3</sub>-CH(CH<sub>3</sub>)-CH[O.] -CH<sub>2</sub>-OH</u>										
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH[O.] -CH <sub>2</sub> -OH + O <sub>2</sub> -> CH <sub>3</sub> -CH(CH <sub>3</sub> )-CO-CH <sub>2</sub> -OH + HO <sub>2</sub>	O <sub>2</sub>	-34.4	2.52e+4	1%	0%	0%	10%	ok		
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH[O.] -CH <sub>2</sub> -OH -> HCO- CH <sub>2</sub> -OH + CH <sub>3</sub> -CH[.] -CH <sub>3</sub>	D	8.1	3.11e+5	8%	15%	29%	50%	Low	<u>kd/kd(R<sub>2</sub>CH.)</u> 2.45	11.26
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH[O.] -CH <sub>2</sub> -OH -> CH <sub>3</sub> - CH(CHO)-CH <sub>3</sub> + HO-CH <sub>2</sub> .	D	7.2	3.50e+6	91%	50%	71%	90%	High		
Based on yields of 2-methyl propanal, acetone, and glycolaldehyde from OH + 3-methyl-1-butene (Atkinson et al, 1998), assuming that OH addition occurs an estimated ~65% of the time at the 1-position relative to total OH addition.										
8 <u>CH<sub>3</sub>-O-CH<sub>2</sub>-O-CH<sub>2</sub>O.</u>										
CH <sub>3</sub> -O-CH <sub>2</sub> -O-CH <sub>2</sub> O. + O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -O-CH <sub>2</sub> -O-CHO	O <sub>2</sub>	-46.6	1.58e+5	96%	70%	84%	100%	ok		
CH <sub>3</sub> -O-CH <sub>2</sub> -O-CH <sub>2</sub> O. -> CH <sub>3</sub> -O-CH <sub>2</sub> O. + HCHO	D	13.3	6.50e+3	4%	0%	16%	30%	ok	<u>kd/kO<sub>2</sub></u> 0.19	0.04
Based on observation of CH <sub>3</sub> -O-CH <sub>2</sub> -O-CHO in 64% yield from dimethoxy methane (Wallington et al, 1997). The 24% yield of CH <sub>3</sub> -O-CO-CH <sub>3</sub> (Wallington et al, 1997) suggests that reaction at the methyl group occurs ~75% of the time. This would mean that decomposition from this radical may be non-negligible.										
9 <u>CH<sub>3</sub>-C(CH<sub>3</sub>)(CH<sub>3</sub>)-O-CH<sub>2</sub>O.</u>										
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH <sub>2</sub> O. + O <sub>2</sub> -> CH <sub>3</sub> - C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CHO + HO <sub>2</sub> .	O <sub>2</sub>	-46.6	1.58e+5	97%	65%	95%	100%	ok		
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH <sub>2</sub> O. -> CH <sub>3</sub> - C[O.](CH <sub>3</sub> )CH <sub>3</sub> + HCHO	D	14.3	3.09e+3	2%	0%	0%	25%	ok		
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH <sub>2</sub> O. -> CH <sub>3</sub> - C(CH <sub>3</sub> )(CH <sub>2</sub> .)-O-CH <sub>2</sub> -OH	I(O)		1.59e+3	1%	0%	0%	25%	ok		
Based on observation of t-butyl formate as the major product from MTBE (Tuazon et al, 1991b; Smith et al, 1991).										
10 <u>CH<sub>3</sub>-CH<sub>2</sub>-O-CH[O.] -CH<sub>3</sub></u>										
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>3</sub> + O <sub>2</sub> -> CH <sub>3</sub> - CH <sub>2</sub> -O-CO-CH <sub>3</sub> + HO <sub>2</sub> .	O <sub>2</sub>	-49.4	3.94e+4	8%	0%	5%	10%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	D	10.1	7.44e+4	16%	0%	0%	15%	High		
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -O- CHO + CH <sub>3</sub> .	D	-4.8	3.54e+5	76%	60%	95%	100%	ok	<u>kd/kO<sub>2</sub></u> 19.00	8.99
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>3</sub> -> CH <sub>3</sub> - CH(OH)-O-CH <sub>2</sub> -CH <sub>2</sub> .	I(O)		5.31e+2	0%	0%	0%	25%	ok		
Based on ethyl formate from diethyl ether in 92% (Wallington and Japar, 1991) or 66% (Eberhard et al, 1993) yields and ethyl acetate in 4% yield (Eberhard et al, 1993) Average of yields for ethyl formate used in computing yield ratio. (Acetaldehyde also observed, but could be formed in other ways)										

Table 33 (continued)

Radical Reaction	Type	$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
			k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
11 <u>CH3-CH2-CH2-CH[O.] -O-CH3</u>										
CH3-CH2-CH2-CH[O.] -O-CH3 + O2 -> HO2. + CH3-CH2-CH2-CO-O-CH3	O2	-49.7	3.94e+4	0%	0%	0%	30%	ok		
CH3-CH2-CH2-CH[O.] -O-CH3 -> CH3-CH2-CH2. + CH3-O-CHO	D	-6.5	1.45e+8	100%	50%	66%	100%	ok		
CH3-CH2-CH2-CH[O.] -O-CH3 -> CH3O. + CH3-CH2-CH2-CHO	D	10.3	6.04e+4	0%	0%	0%	30%	ok		
CH3-CH2-CH2-CH[O.] -O-CH3 -> CH3-O-CH(OH)-CH2-CH2-CH2.	I		1.96e+5	0%	0%	0%	30%	ok		
Based on observations of 43% propionaldehyde and 51% methyl formate from methyl n-butyl ether (Aschmann and Atkinson, 1999). This radical is predicted to be formed ~71% of the time. The observed products account for ~70% of the reaction.										
12 <u>CH3-C(CH3)(CH3)-O-CH[O.] -CH3</u>										
CH3-C(CH3)(CH3)-O-CH[O.] -CH3 + O2 -> CH3-C(CH3)(CH3)O-CO-CH3 + HO2.	O2	-49.4	3.94e+4	9%	0%	17%	25%	ok		
CH3-C(CH3)(CH3)-O-CH[O.] -CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CHO	D	11.1	3.51e+4	8%	0%	0%	20%	ok		
CH3-C(CH3)(CH3)-O-CH[O.] -CH3 -> CH3. + CH3-C(CH3)(CH3)-O-CHO	D	-4.8	3.54e+5	82%	70%	83%	100%	ok		<u>kd/kO2</u> 3.3 9.0
CH3-C(CH3)(CH3)-O-CH[O.] -CH3 -> CH3-C(CH3)(CH2.)-O-CH(OH)CH3	I(O)		1.59e+3	0%	0%	0%	20%	ok		
Based on observed t-butyl formate and t-butyl acetate yields from ETBE (Smith et al, 1992).										
13 <u>CH3-CH(CH3)-O-CH[O.] -CH(CH3)-CH3</u>										
CH3-CH(CH3)-O-CH[O.] -CH(CH3)-CH3 + O2 -> HO2. + CH3-CH(CH3)-O-CO-CH(CH3)-CH3	O2	-49.2	3.94e+4	0%	0%	0%	25%	ok		
CH3-CH(CH3)-O-CH[O.] -CH(CH3)-CH3 -> CH3-CH[O.] -CH3 + CH3-CH(CHO)-CH3	D	11.4	2.75e+4	0%	0%	0%	25%	ok		
CH3-CH(CH3)-O-CH[O.] -CH(CH3)-CH3 -> CH3-CH[.] -CH3 + CH3-CH(CH3)-O-CHO	D	-6.1	1.14e+10	100%	50%	100%	100%	ok		
CH3-CH(CH3)-O-CH[O.] -CH(CH3)-CH3 -> CH3-CH(CH3)-CH(OH)-O-CH(CH2.)-CH3	I(O)		5.31e+2	0%	0%	0%	25%	ok		
Based on observation of 48% yield of t-butyl formate from isobutyl isopropyl ether (Stemmler et al, 1997a). This radical is predicted to be formed ~33% of the time.										

Table 33 (continued)

Radical			$\Delta H_r$	Estimated [a]		Expt. Branching [b]			Fit	k Ratios [d]	
Reaction	Type	(kcal)		k (s <sup>-1</sup> )	%	Min	Exp'd	Max	[c]	Expt	Calc
14 <u>CH3-C[O.](CH3)-O-CH3</u>											
CH3-C[O.](CH3)-O-CH3 -> CH3-O-CO-CH3 + CH3.	D	-6.5	2.51e+6	96%	50%	87%	95%	High	0.15	0.05	$\frac{k_d}{k_d(\text{CH}_3)}$
CH3-C[O.](CH3)-O-CH3 -> CH3-CO-CH3 + CH3O.	D	9.5	1.13e+5	4%	5%	13%	25%	Low			
Based on ratios of methyl acetate to acetone yields from MTBE (Tuazon et al, 1991, Smith et al, 1991)											
15 <u>CH3-C[O.](CH3)-O-CH2-CH3</u>											
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3. + CH3-CH2-O-CO-CH3	D	-6.5	2.51e+6	95%	0%	69%	100%	ok	0.44	0.05	
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-CH2O. + CH3-CO-CH3	D	9.3	1.33e+5	5%	0%	31%	100%	ok			
CH3-C[O.](CH3)-O-CH2-CH3 -> CH3-C(CH3)(OH)-O-CH2-CH2.	I(O)		5.31e+2	0%							
Based on ratios of acetone and ethyl acetate yields from ETBE (Smith et al, 1992), assuming they are all formed from this radical, which is estimated to be formed 5% of the time. (Total yields of both are ~6%). This is uncertain.											
16 <u>CH3-CH(CH3)-O-C[O.](CH3)-CH3</u>											
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-CH[O.]-CH3 + CH3-CO-CH3	D	10.1	7.28e+4	3%	0%		20%	ok			
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3. + CH3-CH(CH3)-O-CO-CH3	D	-6.5	2.51e+6	97%	80%	100%	100%	ok			
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH(CH2.)-CH3	I(O)		1.06e+3	0%	0%		20%	ok			
Based on observations of isopropyl acetate as major product (nearly 100% yield) from di-isopropyl acetate (Wallington et al, 1993).											
17 <u>CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3</u>											
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C[O.](CH3)-CH3 + CH3-CO-CH3	D	10.3	6.27e+4	2%	0%	0%	20%	ok			
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3. + CH3-C(CH3)(CH3)-O-CO-CH3	D	-6.5	2.51e+6	97%	75%	100%	100%	ok			
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(CH2.)-O-C(CH3)(OH)-CH3	I(O)		1.59e+3	0%	0%	0%	20%	ok			
Based on observed 85% yield of isopropyl acetate from di-t-butyl ether (Langer et al, 1996).											



Table 33 (continued)

Radical			$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit	k Ratios [d]	
Reaction	Type			k (s <sup>-1</sup> )	%	Min	Exp'd	Max	[c]	Expt	Calc
18 <u>CH<sub>3</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-O-C[O.] (CH<sub>3</sub>)-CH<sub>3</sub></u>											
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-C[O.] (CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> -CH(CH <sub>2</sub> O.)-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	D	9.3	1.32e+5	5%	0%	18%	40%	ok			
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-C[O.] (CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-CH <sub>3</sub>	D	-6.5	2.51e+6	94%	40%	82%	100%	ok		<u>kd/kd(CH<sub>3</sub>)</u>	0.21 0.05
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-C[O.] (CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-O-CH <sub>2</sub> -C[.] (CH <sub>3</sub> )-CH <sub>3</sub>	I(O)		2.70e+4	1%	0%	0%	30%	ok			
Based on 6% yields of CH <sub>3</sub> -CH(CHO)-CH <sub>3</sub> and 28% of CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-CH <sub>3</sub> from isopropyl isobutyl ether (Stemmler et al, 1997a), assuming that the former is formed from subsequent reactions from this radical. This radical is predicted to be formed ~50% of the time.											
19 <u>CH<sub>3</sub>-CH(CH<sub>3</sub>)-O-CH<sub>2</sub>-C[O.] (CH<sub>3</sub>)-CH<sub>3</sub></u>											
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> -C[O.] (CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> . + CH <sub>3</sub> -CO-CH <sub>3</sub>	D	3.7	6.96e+4	13%	0%	0%	25%	ok			
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> -C[O.] (CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> -CO-CH <sub>3</sub>	D	6.2	1.93e+2	0%	0%	0%	25%				
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> -C[O.] (CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-C[.] (CH <sub>3</sub> )-CH <sub>3</sub>	I(O)		4.81e+5	87%	75%	100%	100%	ok			
Based on observed formation of ~25% of CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-CO-CH <sub>3</sub> from isobutyl isopropyl ether (Stemmler et al, 1997a), which can only be formed by the isomerization reaction. However, this radical is predicted to be formed only ~8% of the time.											
20 <u>CH<sub>3</sub>-CH(OH)-CH[O.] -O-CH<sub>3</sub></u>											
CH <sub>3</sub> -CH(OH)-CH[O.] -O-CH <sub>3</sub> + O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CH(OH)-CO-O-CH <sub>3</sub>	O <sub>2</sub>	-48.5	3.94e+4	0%	0%	0%	15%	ok			
CH <sub>3</sub> -CH(OH)-CH[O.] -O-CH <sub>3</sub> -> CH <sub>3</sub> - CH[.] -OH + CH <sub>3</sub> -O-CHO	D	-9.8	3.14e+13	100%	80%	100%	100%	ok			
CH <sub>3</sub> -CH(OH)-CH[O.] -O-CH <sub>3</sub> -> CH <sub>3</sub> O. + CH <sub>3</sub> -CH(OH)-CHO	D	11.5	2.57e+4	0%	0%	0%	15%	ok			
Based on observation of 59% yield of methyl formate and 56% yield of acetaldehyde from 1-methoxy-2-propanol (Tuazon et al, 1998a). This radical is predicted to be formed ~55% of the time, and the observed products account for ~98% of the overall reaction.											

Table 33 (continued)

Radical			$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit	k Ratios [d]	
Reaction	Type			k (s <sup>-1</sup> )	%	Min	Exp'd	Max	[c]	Expt	Calc
21 <u>CH3-CH[O.] -O-CH2-CH2-OH</u>											
CH3-CH[O.] -O-CH2-CH2-OH + O2 -> HO2. + CH3-CO-O-CH2-CH2-OH	O2		-49.4	3.94e+4	7%	5%	18%	30%	ok	<u>kd/kO2</u> 4.6 9.0	
CH3-CH[O.] -O-CH2-CH2-OH -> CH3. + HCO-O-CH2-CH2-OH	D		-4.8	3.54e+5	64%	70%	82%	100%	Low		
CH3-CH[O.] -O-CH2-CH2-OH -> HO-CH2-CH2O. + CH3-CHO	D		10.1	7.39e+4	13%	0%	0%	25%	ok		
CH3-CH[O.] -O-CH2-CH2-OH -> CH3-CH(OH)-O-CH2-CH[.] -OH	I(O)			8.80e+4	16%	0%	0%	25%	ok		
Based on the observed formation of 36% HO-CH2-CH2-O-CHO and 8% CH3-CO-O-CH2-CH2-OH from 2-ethoxy ethanol (Stemmler et al, 1996). This radical is predicted to be formed ~36% of the time. The observed products account for essentially all the reaction.											
22 <u>CH3-CH2-O-CH[O.] -CH2-OH</u>											
CH3-CH2-O-CH[O.] -CH2-OH + O2 -> HO2. + CH3-CH2-O-CO-CH2-OH	O2		-48.3	3.94e+4	0%	0%	0%	25%	ok		
CH3-CH2-O-CH[O.] -CH2-OH -> CH3-CH2O. + HCO-CH2-OH	D		11.5	2.48e+4	0%	0%	0%	25%	ok		
CH3-CH2-O-CH[O.] -CH2-OH -> HO-CH2. + CH3-CH2-O-CHO	D		-6.1	6.36e+10	100%	75%	100%	100%	ok		
Based on the observed formation of ~43% ethyl formate from 2-ethoxy ethanol (Stemmler et al, 1996). This radical is predicted to be formed ~36% of the time. The observed products account for essentially all the reaction.											
23 <u>CH3-CH(CH3)-O-CH[O.] -CH2-OH</u>											
CH3-CH(CH3)-O-CH[O.] -CH2-OH + O2 -> HO2. + CH3-CH(CH3)-O-CO-CH2-OH	O2		-48.3	3.94e+4	0%	0%	0%	15%	ok		
CH3-CH(CH3)-O-CH[O.] -CH2-OH -> CH3-CH[O.] -CH3 + HCO-CH2-OH	D		12.4	1.36e+4	0%	0%	0%	15%	ok		
CH3-CH(CH3)-O-CH[O.] -CH2-OH -> HO-CH2. + CH3-CH(CH3)-O-CHO	D		-6.1	6.36e+10	100%	80%	100%	100%	ok		
CH3-CH(CH3)-O-CH[O.] -CH2-OH -> CH3-CH(CH2.) -O-CH(OH)-CH2-OH	I(O)			1.06e+3	0%	0%	0%	15%	ok		
Based on formation of 57% isopropyl formate from 2-isopropoxy ethanol (Aschmann and Atkinson, 1999). This radical is predicted to be formed ~30% of the time, and the observed products account for essentially all the reaction routes.											

Table 33 (continued)

Radical Reaction	Type	$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
			k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
24 <u>CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH[O.]</u> -O-CH <sub>2</sub> -CH <sub>2</sub> -OH										
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -O-CH <sub>2</sub> -CH <sub>2</sub> -OH + O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	O2	-49.7	3.94e+4	0%	0%	0%	25%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> . + HCO-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	D	-6.5	1.45e+8	100%	50%	100%	100%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> HO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CHO	D	10.1	7.06e+4	0%	0%	0%	25%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> HO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	I		1.96e+5	0%	0%	0%	25%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-O-CH <sub>2</sub> -CH[.] -OH	I(O)		8.80e+4	0%	0%	0%	25%	ok		

Based on observations of propionaldehyde and HO-CH<sub>2</sub>-CH<sub>2</sub>-O-CHO in ~20% yields from 2-butoxy ethanol by Tuazon et al. (1998), with somewhat higher yields observed by Stemmler et al. (1997b). This radical is believed to be formed ~20% of the time.

25 <u>CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH[O.]</u> -CH <sub>2</sub> -OH										
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>2</sub> -OH + O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -OH	O2	-48.3	3.94e+4	0%	0%	0%	25%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> O. + HCO-CH <sub>2</sub> -OH	D	11.6	2.46e+4	0%	0%	0%	25%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>2</sub> -OH -> HO-CH <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CHO	D	-6.1	6.36e+10	100%	80%	100%	100%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH <sub>2</sub> -CH[.] -CH <sub>2</sub> -O-CH(OH)-CH <sub>2</sub> -OH	I(O)		1.83e+4	0%	0%	0%	25%	ok		

Based on observations of n-butyl formate from 2-butoxy ethanol with yields of 57% (Tuazon et al, 1998) or ~35% (Stemmler et al., 1997b). This radical is believed to be formed ~50% of the time.

Table 33 (continued)

Radical		$\Delta H_r$	Estimated [a]		Expt. Branching [b]			Fit	k Ratios [d]	
Reaction	Type	(kcal)	k (s <sup>-1</sup> )	%	Min	Exp'd	Max	[c]	Expt	Calc
26 <u>CH<sub>3</sub>-C[O.](CH<sub>3</sub>)-O-CH<sub>2</sub>-CH<sub>2</sub>-OH</u>										
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>2</sub> -OH → CH <sub>3</sub> . + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	D	-6.5	2.51e+6	92%	60%	90%	100%	ok		
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>2</sub> -OH → HO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CO-CH <sub>3</sub>	D	9.3	1.32e+5	5%	0%	0%	20%	ok		
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>2</sub> -OH → CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-O-CH <sub>2</sub> -CH[.]-OH	I(O)		8.80e+4	3%	0%	0%	20%	ok		
Based on formation of 44% CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -OH from 2-isopropoxy ethanol (Aschmann and Atkinson, 1999). This radical is predicted to be formed ~50% of the time, and the observed products account for essentially all the reaction routes.										
27 <u>CH<sub>3</sub>-C(CH<sub>3</sub>)(OH)-CH<sub>2</sub>-O-C[O.](CH<sub>3</sub>)-CH<sub>3</sub></u>										
CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> → CH <sub>3</sub> -C(OH)(CH <sub>2</sub> O.)-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	D	9.3	1.32e+5	5%	0%	0%	25%	ok		
CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> → CH <sub>3</sub> . + CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-CO-CH <sub>3</sub>	D	-6.5	2.51e+6	95%	75%	100%	100%	ok		
Based on observed formation of ~25% of CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-CO-CH <sub>3</sub> from isobutyl isopropyl ether (Stemmler et al, 1997a), which can only be formed by this reaction. However, this radical is predicted to be formed only ~5% of the time.										
28 <u>CH<sub>3</sub>-CO-CH<sub>2</sub>O.</u>										
CH <sub>3</sub> -CO-CH <sub>2</sub> O. + O <sub>2</sub> → CH <sub>3</sub> -CO-CHO + HO <sub>2</sub> .	O <sub>2</sub>	-26.9	1.01e+4	0%	0%		25%	ok		
CH <sub>3</sub> -CO-CH <sub>2</sub> O. → HCHO + CH <sub>3</sub> -CO.	D	2.6	1.74e+9	94%	75%	100%	100%	ok		
Based on data of Jenkin et al (1993) indicating that decomposition dominates.										
29 <u>CH<sub>3</sub>-CH<sub>2</sub>-O-CO-CH<sub>2</sub>O.</u>										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> O. + O <sub>2</sub> → CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CHO + HO <sub>2</sub> .	O <sub>2</sub>	-23.3	3.23e+3	14%	30%	<u>75%</u>	100%	Low		
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> O. → HCHO + CH <sub>3</sub> -CH <sub>2</sub> -O-CO.	D	13.5	1.39e+1	0%	0%	<u>0%</u>	70%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> O. → CH <sub>3</sub> -CH[.]-O-CO-CH <sub>2</sub> -OH	I(O)		1.99e+4	86%	0%	<u>25%</u>	70%	High		
The most reasonable explanation for the observation of ~25% of CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CHO from ethyl 3-ethoxypropionate (Baxley et al, 1997) is to assume that this radical reacts with O <sub>2</sub> to a significant extent. This radical is predicted to be formed ~33% of the time.										

Table 33 (continued)

Radical Reaction	Type	$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
			k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
30 <u>CH<sub>3</sub>-CH(CH<sub>2</sub>O.)-O-CO-CH<sub>3</sub></u>										
CH <sub>3</sub> -CH(CH <sub>2</sub> O.)-O-CO-CH <sub>3</sub> + O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CH(CHO)-O-CO-CH <sub>3</sub>	O <sub>2</sub>	-30.8	3.37e+4	41%	0%	0%	75%	ok		
CH <sub>3</sub> -CH(CH <sub>2</sub> O.)-O-CO-CH <sub>3</sub> -> CH <sub>3</sub> -CO-O-CH[.] -CH <sub>3</sub> + HCHO	D	12.8	4.93e+4	59%	25%	100%	100%	ok		
Necessary to assume decomposition is non-negligible to explain observation of acetic acid as a 9% product from isopropyl acetate (Tuazon et al, 1998b).										
31 <u>CH<sub>3</sub>-CH<sub>2</sub>-CH[O.] -CH<sub>2</sub>-O-CO-CH<sub>3</sub></u>										
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>2</sub> -O-CO-CH <sub>3</sub> + O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -CO-CH <sub>2</sub> -O-CO-CH <sub>3</sub>	O <sub>2</sub>	-34.8	2.91e+4	89%	25%	50%	100%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>2</sub> -O-CO-CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> . + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CHO	D	8.4	2.15e+3	7%	0%		75%	ok		
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>2</sub> -O-CO-CH <sub>3</sub> -> CH <sub>3</sub> -CO-O-CH <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -CHO	D	8.8	1.57e+3	5%	0%		75%	ok		
Based on observed formation of ~15% CH <sub>3</sub> -CH <sub>2</sub> -CO-CH <sub>2</sub> -O-CO-CH <sub>3</sub> from n-butyl acetate (Veillerot et al. 1995). This radical predicted to be formed ~30% of the time. Only ~30% of the reaction route are accounted for, and the yields are only approximate.										
32 <u>CH<sub>3</sub>-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-CH[O.] -CH<sub>3</sub></u>										
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>3</sub> + O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CO-CH <sub>3</sub>	O <sub>2</sub>	-36.0	3.94e+4	62%	25%	65%	100%	ok		
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>3</sub> -> CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> . + CH <sub>3</sub> -CHO	D	5.2	2.41e+4	38%	0%	35%	75%	ok		
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -CHO	D	7.9	2.76e+1	0%	0%		75%			
Based on observed formation of ~15% CH <sub>3</sub> -CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CO-CH <sub>3</sub> from n-butyl acetate (Veillerot et al. 1995). This radical predicted to be formed ~23% of the time. Only ~30% of the reaction route are accounted for, and the yields are only approximate.										
33 <u>CH<sub>3</sub>-O-CO-CH<sub>2</sub>-CH[O.] -CO-O-CH<sub>3</sub></u>										
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH[O.] -CO-O-CH <sub>3</sub> + O <sub>2</sub> -> CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CO-CO-O-CH <sub>3</sub> + HO <sub>2</sub> .	O <sub>2</sub>	-30.2	6.90e+3	76%	0%	<u>10%</u>	10%	High		
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH[O.] -CO-O-CH <sub>3</sub> -> CH <sub>3</sub> -O-CO-CHO + CH <sub>3</sub> -O-CO-CH <sub>2</sub> .	D	16.7	4.48e+0	0%	0%	<u>0%</u>	10%	ok		
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH[O.] -CO-O-CH <sub>3</sub> -> CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CHO + CH <sub>3</sub> -O-CO.	D	7.3	1.37e+3	15%	0%	<u>0%</u>	20%	ok		
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH[O.] -CO-O-CH <sub>3</sub> -> CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH(OH)-CO-O-CH <sub>2</sub> .	I(OCO)		7.88e+2	9%	80%	<u>90%</u>	100%	Low		
It is necessary to assume that the isomerization of this radical dominates in order for model calculations to approximately fit results of DBE-4 reactivity experiments. The reaction with O <sub>2</sub> , which is predicted to be the most important competing route, is arbitrarily assumed to occur ~10% of the time.										

Table 33 (continued)

Radical Reaction	Type	$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
			k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
34 <u>CH3-CH2-O-CH[O.]-CH2-O-CO-CH3</u>										
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 + O2 -> HO2. + CH3-CH2-O-CO-CH2-O-CO-CH3	O2	-48.3	3.94e+4	0%	0%	0%	30%	ok		
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CH2O. + CH3-CO-O-CH2-CHO	D	11.5	2.48e+4	0%	0%	0%	30%	ok		
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CO-O-CH2. + CH3-CH2-O-CHO	D	-3.6	1.63e+7	100%	50%	90%	100%	ok		
CH3-CH2-O-CH[O.]-CH2-O-CO-CH3 -> CH3-CO-O-CH2-CH(OH)-O-CH2-CH2.	I(OCO)		5.31e+2	0%	0%	0%	30%	ok		

Based on observed yield of ethyl formate (33%) from 2-ethoxyethyl acetate (Wells et al., 1996). This is somewhat lower than the predicted 44% formation for this radical, but within the uncertainty of the estimate.

35 <u>CH<sub>3</sub>-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH[O.] -CH<sub>3</sub></u>										
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>3</sub> + O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CO-CH <sub>3</sub>	O <sub>2</sub>	-49.4	3.94e+4	8%	5%	10%	25%	ok		
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>3</sub> -> CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	D	10.1	7.39e+4	15%	0%	0%	25%	ok		
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CHO	D	-4.8	3.54e+5	72%	50%	90%	100%	ok	<u>kd/kO<sub>2</sub></u>	9.3 9.0
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -CH <sub>3</sub> -> CH <sub>3</sub> -CH(OH)-O-CH <sub>2</sub> -CH[.] -O-CO-CH <sub>3</sub>	I(O)		2.72e+4	6%	0%	0%	25%	ok		

Based on yields of CH<sub>3</sub>-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-O-CHO (37%) and CH<sub>3</sub>-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-CH<sub>3</sub> (4%) from 2-ethoxyethyl acetate (Wells et al, 1996). This radical is predicted to be formed ~36% of the time, which is consistent with these product yields.

Table 33 (continued)

Radical Reaction	Type	$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
			k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
36 <u>CH<sub>3</sub>-CH<sub>2</sub>-O-CO-CH<sub>2</sub>-CH[O.]</u> -O-CH <sub>2</sub> -CH <sub>3</sub>										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH[O.]	O2	-51.8	3.94e+4	0%	0%	0%	20%	ok		
+ O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CO- O-CH <sub>2</sub> -CH <sub>3</sub>										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH[O.]	D	-5.8	8.34e+7	100%	50%	84%	100%	ok		
-> CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O- CHO										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH[O.]	D	8.0	3.46e+5	0%	0%	16%	20%	ok		
-> CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> - CHO										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH[O.]	I(O)		5.31e+2	0%	0%	0%	20%	ok		
-> CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH(OH)-O-CH <sub>2</sub> - CH <sub>2</sub> .										

Based on yield ratios for ethyl formate and CH<sub>3</sub>-CH<sub>2</sub>-O-CO-CH<sub>2</sub>-CHO from ethyl 3-ethoxypropionate (Baxley et al, 1997). Total yield is ~42%, while predicted amount of this radical formed is ~50%.

37 <u>CH<sub>3</sub>-CH<sub>2</sub>-O-CO-CH<sub>2</sub>-CH<sub>2</sub>-O-CH[O.]</u> -CH <sub>3</sub>										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]	O2	-49.4	3.94e+4	8%	0%	0%	50%	ok		
+ O <sub>2</sub> -> HO <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> - O-CO-CH <sub>3</sub>										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]	D	10.1	7.39e+4	16%	0%	0%	50%	ok		
-> CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> - CHO										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]	D	-4.8	3.54e+5	75%	50%	75%	100%	ok		
-> CH <sub>3</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O- CHO										
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]	I(O)		2.32e+3	0%	0%	0%	50%	ok		
-> CH <sub>3</sub> -CH(OH)-O-CH <sub>2</sub> -CH[.]										
-CO-O-CH <sub>2</sub> - CH <sub>3</sub>										

Based on formation of 30% CH<sub>3</sub>-CH<sub>2</sub>-O-CO-CH<sub>2</sub>-CH<sub>2</sub>-O-CHO from ethyl 3-ethoxypropionate (Baxley et al, 1977). Note that this radical is predicted to be formed 40% of the time, so the observed yield is higher than maximum predicted.

38 <u>CH<sub>3</sub>-C[O.]</u> (CHO)-CH <sub>2</sub> -OH										
CH <sub>3</sub> -C[O.]	D	19.0	7.13e-3	0%	0%	0%	25%	ok		
(CHO)-CH <sub>2</sub> -OH -> HCO-CO- CH <sub>2</sub> -OH + CH <sub>3</sub> .										
CH <sub>3</sub> -C[O.]	D	-0.7	1.53e+7	94%	75%	100%	100%			
(CHO)-CH <sub>2</sub> -OH -> CH <sub>3</sub> -CO- CH <sub>2</sub> -OH + HCO.										
CH <sub>3</sub> -C[O.]	D	8.9	9.82e+5	6%	0%	0%	25%	ok		
(CHO)-CH <sub>2</sub> -OH -> CH <sub>3</sub> -CO- CHO + HO-CH <sub>2</sub> .										

Based on observations of hydroxyacetone as a major product in the reaction of OH with methacrolein (Tuazon and Atkinson, 1990). This and products from other radicals formed believed to account for all the reaction routes.

Table 33 (continued)

Radical	Reaction	Type	$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
				k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
39	<u>CH3-C[O.](CH3)-CO-O-CH3</u>										
	CH3-C[O.](CH3)-CO-O-CH3 -> CH3-O-CO-CO-CH3 + CH3.	D	12.2	1.16e+0	0%	0%	0%	50%	ok		
	CH3-C[O.](CH3)-CO-O-CH3 -> CH3-CO-CH3 + CH3-O-CO.	D	5.7	4.62e+3	85%	50%	100%	100%	ok		
	CH3-C[O.](CH3)-CO-O-CH3 -> CH3-C(CH3)(OH)-CO-O-CH2.	I(O)		7.88e+2	15%	0%	0%	50%	ok		
It is necessary to assume that the decomposition to CH3-O-CO. is a major route in order for model to simulate results of methyl isobutyrate reactivity experiments (Carter et al, 1999a).											
40	<u>CH3-C[O.](CH3)-O-CO-CH3</u>										
	CH3-C[O.](CH3)-O-CO-CH3 -> CH3-CO-O-CO-CH3 + CH3.	D [e]	10.0	3.48e+2	66%	50%	<u>76%</u>	90%	ok	<u>kd/kd(CH3)</u> 0.32 0.31	
	CH3-C[O.](CH3)-O-CO-CH3 -> CH3-CO-CH3 + CH3-CO2.	D	10.7	1.09e+2	21%	10%	<u>24%</u>	50%	ok		
	CH3-C[O.](CH3)-O-CO-CH3 -> CH3-C(CH3)(OH)-O-CO-CH2.	I(OCO)		6.72e+1	13%	0%	<u>0%</u>	25%	ok		
Based on yields of acetone and acetic anhydride from isopropyl acetate and t-butyl acetate (Tuazon et al. 1998b).											
41	<u>CH3-CO-CH2-CH[O.]-CH3</u>										
	CH3-CO-CH2-CH[O.]-CH3 + O2 -> CH3-CO-CH2-CO-CH3 + HO2.	O2	-38.1	3.94e+4	38%	10%	<u>19%</u>	30%	High	<u>kd/kO2</u> 4.3 1.6	
	CH3-CO-CH2-CH[O.]-CH3 -> CH3-CHO + CH3-CO-CH2.	D	3.9	6.37e+4	62%	70%	<u>81%</u>	90%	Low		
	CH3-CO-CH2-CH[O.]-CH3 -> CH3-CO-CH2-CHO + CH3.	D	5.8	1.35e+2	0%	0%	<u>0%</u>	10%	ok		
	CH3-CO-CH2-CH[O.]-CH3 -> CH3-CH(OH)-CH2-CO-CH2.	I(CO)		2.53e+2	0%	0%	<u>0%</u>	10%	ok		
Based on ratios of acetaldehyde to 2,4-pentadione yields from OH + 2-pentanone (Atkinson et al, 1999b).											
44	<u>CH3-O-CO-CH2-CH[O.]-CH2-CO-O-CH3</u>										
	CH3-O-CO-CH2-CH[O.]-CH2-CO-O-CH3 + O2 -> CH3-O-CO-CH2-CO-CH2-CO-O-CH3 + HO2.	O2	-40.5	3.94e+4	38%	90%	<u>100%</u>	100%	Low		
	CH3-O-CO-CH2-CH[O.]-CH2-CO-O-CH3 -> CH3-O-CO-CH2-CHO + CH3-O-CO-CH2.	D	4.8	6.34e+4	62%	0%	<u>0%</u>	10%	High		
Necessary to assume that reaction with O2 dominates for model simulations of dimethyl glutarate (DBE-5) chamber experiments. The observation of CH3-O-CO-CH2-CO-CH2-CO-O-CH3 as a product of the OH + DBE-5 reaction (Tuazon et al, 1999) also indicates that the O2 reaction is important.											



Table 33 (continued)

Radical		$\Delta H_r$ (kcal)	Estimated [a]		Expt. Branching [b]			Fit [c]	k Ratios [d]	
Reaction	Type		k (s <sup>-1</sup> )	%	Min	Exp'd	Max		Expt	Calc
45 <u>CH<sub>3</sub>-O-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH[O.]</u> -CO-O-CH <sub>3</sub>										
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]	O <sub>2</sub>	-28.1	3.57e+3	77%	0%	<u>10%</u>	10%	High		
+ O <sub>2</sub> -> CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CO-CO-O-CH <sub>3</sub> + HO <sub>2</sub> .										
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]	D	15.0	1.67e+1	0%	0%	<u>0%</u>	10%	ok		
-> CH <sub>3</sub> -O-CO-CHO + CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> .										
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]	D	9.5	2.80e+2	6%	0%	<u>0%</u>	10%	ok		
-> CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CHO + CH <sub>3</sub> -O-CO.										
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]	I(OCO)		7.88e+2	17%	80%	<u>90%</u>	100%	Low		
-> CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-CO-O-CH <sub>2</sub> .										
Isomerization is assumed to dominate by analogy with the assumptions made for CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH[O.]										
CO-O-CH <sub>3</sub> radicals. This also results in somewhat better fits of model simulations to dimethyl glutarate										
(DBE-5) reactivity experiments. Reaction with O <sub>2</sub> , predicted to be the major competing process, is arbitrarily										
assumed to occur ~10% of the time.										
46 <u>*C[O.](CH<sub>3</sub>)-CH<sub>2</sub>-O-CO-O-*</u>										
*C[O.](CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-O-*	D [e]	11.1	7.40e+1	0%	0%	0%	20%	ok		
-> *CH <sub>2</sub> -O-CO-O-CO-*										
+ CH <sub>3</sub> .										
*C[O.](CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-O-*	D [e]	4.9	8.61e+5	99%	75%	100%	100%	ok		
-> CH <sub>3</sub> -CO-O-CO-O-CH <sub>2</sub> .										
*C[O.](CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-O-*	D	5.6	5.12e+3	1%	0%	0%	20%	ok		
-> CH <sub>3</sub> -CO-CH <sub>2</sub> -O-CO <sub>2</sub> .										
Necessary to assume that the decomposition to CH <sub>3</sub> -CO-O-CO-O-CH <sub>2</sub> . dominates in order for model to fit										
results of propylene carbonate reactivity chamber experiments.										

- [a] Rate constants estimated for T=298K using recommended parameters as discussed in the text. Units are sec<sup>-1</sup>. Unimolecular rate constants for O<sub>2</sub> reaction calculated assuming [O<sub>2</sub>] = 5.18 x 10<sup>-18</sup> molec cm<sup>-3</sup>. "%" is the estimated percentage of the radical which reacts with this reaction.
- [b] Minimum, expected, and maximum fractions for this reaction route relative to all reactions of this radical, based on analysis of the experimental data. Minimum and maximum values are subjective estimates. Underlined branching ratios are used for explicit estimates for this radical -- overriding the temperature-dependent rate constant estimates.
- [c] "High" means that the estimated branching ratio is greater than the maximum value estimated from analysis of the experimental data; "Low" means that the estimated ratio is lower than the minimum; "ok" means that the estimated branching ratio lies between the minimum and maximum considered consistent with the experimental data.
- [d] Rate constant ratios which can be used for quantitative rate constant estimates.
- [e] The activation energy is reduced by 2 kcal/mole for reactions that form products with -CO-O-CO- groups. If this correction were not applied, the estimated rate constant would be a factor of ~30 lower.

Table 33 also includes the heats of reaction for the various reactions where relevant and the estimated rate constants and corresponding branching ratios for the competing reactions. (The predictions for the O<sub>2</sub> reactions and the isomerizations are as discussed in the previous section, the predictions for the decompositions are discussed below.) An indication of how well the predicted branching ratios agree with the observed ratios is also shown. Table 34 gives a subset of the information on Table 33, organized by alkoxy reaction type rather than by radical. This is useful for obtaining an indication of how well the estimates are performing for a particular type of reaction. For that reason, Table 34 includes results using several alternative assumptions, as discussed where applicable below.

Table 34. Experimental and estimated branching ratios for radicals where relevant data are available, sorted by type of reaction. Estimated branching ratios derived using alternative mechanistic assumptions are also shown.

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated k (min <sup>-1</sup> )	%	Expt. Fract React. Min Exp'd Max	Estimation vs Experimental
<u>Estimates using Recommended Parameters</u>						
<u>Decomposition Forming CH<sub>3</sub>.</u>						
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CO-CH <sub>3</sub> -> CH <sub>3</sub> -CO-O-CO-CH <sub>3</sub> + CH <sub>3</sub> .	0	9.99	3.48e+2	66%	50% 76% 90%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -O-CHO + CH <sub>3</sub> .	0	-4.81	3.54e+5	76%	60% 95% 100%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CHO	0	-4.81	3.54e+5	82%	70% 83% 100%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CHO	0	-4.81	3.54e+5	75%	50% 75% 100%	ok
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CHO	0	-4.81	3.54e+5	72%	50% 90% 100%	ok
CH <sub>3</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> CH <sub>3</sub> . + HCO-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	0	-4.81	3.54e+5	64%	70% 82% 100%	Low: 64% vs 70%
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>3</sub> -> CH <sub>3</sub> -O-CO-CH <sub>3</sub> + CH <sub>3</sub> .	0	-6.51	2.51e+6	96%	50% 87% 95%	High: 96% vs 95%
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CO-CH <sub>3</sub>	0	-6.51	2.51e+6	97%	80% 100% 100%	ok
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>3</sub>	0	-6.51	2.51e+6	95%	0% 69% 100%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CO-CH <sub>3</sub>	0	-6.51	2.51e+6	97%	75% 100% 100%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-CO-CH <sub>3</sub>	0	-6.51	2.51e+6	94%	40% 82% 100%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> . + CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-CO-CH <sub>3</sub>	0	-6.51	2.51e+6	95%	75% 100% 100%	ok
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> CH <sub>3</sub> . + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	0	-6.51	2.51e+6	92%	60% 90% 100%	ok
<u>Decomposition Forming RCH<sub>2</sub>.</u>						
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> -CHO + CH <sub>3</sub> -CH <sub>2</sub> .	0	6.94	6.46e+3	14%	24% 36% 54%	Low: 14% vs 24%
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]-CH <sub>2</sub> -CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -CHO + CH <sub>3</sub> -CH <sub>2</sub> .	0	6.71	1.53e+4	28%	26% 39% 58%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]-O-CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> . + CH <sub>3</sub> -O-CHO	0	-6.54	1.45e+8	100%	50% 66% 100%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> . + HCO-O-CH <sub>2</sub> -CH <sub>2</sub> -OH	0	-6.54	1.45e+8	100%	50% 100% 100%	ok
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> . + CH <sub>3</sub> -CHO	0	5.17	2.41e+4	38%	0% 35% 75%	ok
<u>Decomposition Forming R<sub>2</sub>CH.</u>						
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH[O.]-CH(CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> -CH[.]-CH <sub>3</sub> + CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CHO	0	-6.09	1.14e+10	100%	50% 100% 100%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated k (min <sup>-1</sup> )	%	Expt. Min	Fract Exp'd	React. Max	Estimation vs Experimental
<u>Decomposition Forming R3C.</u>								
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> O.)-CH <sub>3</sub> -> HCHO + CH <sub>3</sub> -C[O.](CH <sub>3</sub> ) CH <sub>3</sub>	0	10.40	1.31e+6	98%	75%	98%	100%	ok
<u>Decomposition Forming RO. (Rate constants estimated to minimize bias [Equation (XX)].</u>								
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )O-CH <sub>2</sub> O. -> CH <sub>3</sub> -C[O.](CH <sub>3</sub> )CH <sub>3</sub> + HCHO	0	14.34	3.09e+3	2%	0%	0%	25%	ok
CH <sub>3</sub> -O-CH <sub>2</sub> -O-CH <sub>2</sub> O. -> CH <sub>3</sub> -O-CH <sub>2</sub> O. + HCHO	0	13.34	6.50e+3	4%	0%	16%	30%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH[O.]-CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH[O.]- CH <sub>3</sub> + HCO-CH <sub>2</sub> -OH	0	12.35	1.36e+4	0%	0%	0%	15%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH <sub>2</sub> - CH <sub>2</sub> -CH <sub>2</sub> O. + HCO-CH <sub>2</sub> -OH	0	11.55	2.46e+4	0%	0%	0%	25%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -O-CO-CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CHO	0	11.54	2.48e+4	0%	0%	0%	30%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -OH -> CH <sub>3</sub> -CH <sub>2</sub> O. + HCO- CH <sub>2</sub> -OH	0	11.54	2.48e+4	0%	0%	0%	25%	ok
CH <sub>3</sub> -CH(OH)-CH[O.]-O-CH <sub>3</sub> -> CH <sub>3</sub> O. + CH <sub>3</sub> - CH(OH)-CHO	0	11.49	2.57e+4	0%	0%	0%	15%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> - C[O.](CH <sub>3</sub> )-CH <sub>3</sub> + CH <sub>3</sub> -CHO	0	11.07	3.51e+4	8%	0%	0%	20%	ok
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CO-CH <sub>3</sub> -> CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> - CO <sub>2</sub> .	0	10.73	1.09e+2	21%	10%	24%	50%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]-O-CH <sub>3</sub> -> CH <sub>3</sub> O. + CH <sub>3</sub> -CH <sub>2</sub> - CH <sub>2</sub> -CHO	0	10.34	6.04e+4	0%	0%	0%	30%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> - C[O.](CH <sub>3</sub> )-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	10.29	6.27e+4	2%	0%	0%	20%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> HO-CH <sub>2</sub> - CH <sub>2</sub> O. + CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CHO	0	10.13	7.06e+4	0%	0%	0%	25%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> -CH[O.]- CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	10.09	7.28e+4	3%	0%	0%	20%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> - CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	0	10.07	7.39e+4	16%	0%	0%	50%	ok
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> -CO-O- CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	0	10.07	7.39e+4	15%	0%	0%	25%	ok
CH <sub>3</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> HO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	0	10.07	7.39e+4	13%	0%	0%	25%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> -> CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	0	10.06	7.44e+4	16%	0%	0%	15%	High: 16% vs 15%
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>3</sub> -> CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> O.	0	9.50	1.13e+5	4%	5%	13%	25%	Low: 4% vs 5%
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> - CH(CH <sub>2</sub> O.)-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	9.29	1.32e+5	5%	0%	18%	40%	ok
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>2</sub> -OH -> HO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	9.29	1.32e+5	5%	0%	0%	20%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> -> CH <sub>3</sub> - C(OH)(CH <sub>2</sub> O.)-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	9.29	1.32e+5	5%	0%	0%	25%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated k (min <sup>-1</sup> )	%	Expt. Fract React. Min Exp'd Max	Estimation vs Experimental
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	9.28	1.33e+5	5%	0% 31% 100%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CHO	0	7.99	3.46e+5	0%	0% 16% 20%	ok
<u>Decomposition Forming RCO.</u>						
CH <sub>3</sub> -CO-CH <sub>2</sub> O. → HCHO + CH <sub>3</sub> -CO.	0	2.59	1.74e+9	94%	75% 100% 100%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> O. → HCHO + CH <sub>3</sub> -CH <sub>2</sub> -O-CO.	0	13.50	1.39e+1	0%	0% 0% 70%	ok
<u>Decomposition forming HCO.</u>						
CH <sub>3</sub> -C[O.](CHO)-CH <sub>2</sub> -OH → CH <sub>3</sub> -CO-CH <sub>2</sub> -OH + HCO.	0	-0.66	1.53e+7	94%	75% 100% 100%	ok
<u>Decomposition Forming a-Hydroxy Radicals</u>						
HO-CH <sub>2</sub> -CH <sub>2</sub> O. → HO-CH <sub>2</sub> . + HCHO	0	11.79	1.11e+5	78%	70% 78% 85%	ok
CH <sub>3</sub> -CH[O.]-CH <sub>2</sub> -OH → HO-CH <sub>2</sub> . + CH <sub>3</sub> -CHO	0	6.62	5.19e+6	99%	85% 100% 100%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH[O.]-CH <sub>2</sub> -OH → CH <sub>3</sub> -CH(CHO)-CH <sub>3</sub> -CH(OH)-CH[O.]-CH <sub>3</sub> → CH <sub>3</sub> -CHO + CH <sub>3</sub> -CH[.]-OH	0	7.15	3.50e+6	91%	50% 71% 90%	High: 91% vs 90%
	0	2.87	2.56e+9	100%	100% 100% 100%	
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -OH → HO-CH <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CHO	0	-6.05	6.36e+10	100%	80% 100% 100%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH[O.]-CH <sub>2</sub> -OH → HO-CH <sub>2</sub> . + CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CHO	0	-6.05	6.36e+10	100%	80% 100% 100%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -OH → HO-CH <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O-CHO	0	-6.05	6.36e+10	100%	75% 100% 100%	ok
CH <sub>3</sub> -CH(OH)-CH[O.]-O-CH <sub>3</sub> → CH <sub>3</sub> -CH[.]-OH + CH <sub>3</sub> -O-CHO	0	-9.80	3.14e+13	100%	80% 100% 100%	ok
<u>Decompositions Forming ROCH<sub>2</sub>.</u>						
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> -C[O.](CH <sub>3</sub> )-CH <sub>3</sub> → CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> . + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	3.74	6.96e+4	13%	0% 0% 25%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH[O.]-CH <sub>2</sub> -O-CO-CH <sub>3</sub> → CH <sub>3</sub> -CO-O-CH <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -CHO	0	8.84	1.57e+3	5%	0% 75%	ok
<u>Decompositions Forming ROCH[.]R</u>						
CH <sub>3</sub> -CH(CH <sub>2</sub> O.)-O-CO-CH <sub>3</sub> → CH <sub>3</sub> -CO-O-CH[.]-CH <sub>3</sub> + HCHO	0	12.81	4.93e+4	59%	25% 100% 100%	ok
<u>Decomposition Forming RO-CO-CH<sub>2</sub>. or R-CO-O-CH<sub>2</sub>.</u>						
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O-CHO	0	-5.80	8.34e+7	100%	50% 84% 100%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -O-CO-CH <sub>3</sub> → CH <sub>3</sub> -CO-O-CH <sub>2</sub> . + CH <sub>3</sub> -CH <sub>2</sub> -O-CHO	0	-3.60	1.63e+7	100%	50% 90% 100%	ok
<u>Decompositions forming RO-CO.</u>						
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-CO-O-CH <sub>3</sub> → CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> -O-CO.	0	5.69	4.62e+3	85%	50% 100% 100%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> O. → HCHO + CH <sub>3</sub> -CH <sub>2</sub> -O-CO.	0	13.50	1.39e+1	0%	0% 0% 70%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated k (min <sup>-1</sup> )	%	Expt. Min	Fract Exp'd	React. Max	Estimation vs Experimental
CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH[O.] -> CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CHO + CH <sub>3</sub> -O-CO.	0	7.33	1.37e+3	15%	0%	0%	20%	ok
<u>Isomerizations (no -O- or -CO- in transition state ring)</u>								
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -> HO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	0		1.96e+5	0%	0%	0%	25%	ok
<u>Isomerizations with -O- or -CO- in transition state ring (3.5 kcal/mole strain energy assumed)</u>								
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.] -> CH <sub>3</sub> -CH(OH)-O-CH <sub>2</sub> -CH <sub>2</sub> .	0		5.31e+2	0%	0%	0%	25%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )O-CH <sub>2</sub> O. -> CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> )O-CH <sub>2</sub> -OH	0		1.59e+3	1%	0%	0%	25%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )O-CH[O.] -> CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> )O-CH(OH)CH <sub>3</sub>	0		1.59e+3	0%	0%	0%	20%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-C[O.] -> CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-O-CH(CH <sub>2</sub> .)-CH <sub>3</sub>	0		1.06e+3	0%	0%	0%	20%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-C[O.] -> CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>2</sub> .)-O-C(CH <sub>3</sub> )(OH)-CH <sub>3</sub>	0		1.59e+3	0%	0%	0%	20%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH[O.] -> CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH(OH)-O-CH <sub>2</sub> -CH <sub>2</sub> .	0		5.31e+2	0%	0%	0%	20%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -> CH <sub>3</sub> -CH(OH)-O-CH <sub>2</sub> -CH[.] -> CO-O-CH <sub>2</sub> -CH <sub>3</sub>	0		2.32e+3	0%	0%	0%	50%	ok
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -> CH <sub>3</sub> -CH(OH)-O-CH <sub>2</sub> -CH[.] -> O-CO-CH <sub>3</sub>	0		2.72e+4	6%	0%	0%	25%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -> CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-O-CH <sub>2</sub> -CH[.] -> OH	0		8.80e+4	0%	0%	0%	25%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.] -> CH <sub>3</sub> -CH <sub>2</sub> -CH[.] -> CH <sub>2</sub> -O-CH(OH)-CH <sub>2</sub> -OH	0		1.83e+4	0%	0%	0%	25%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.] -> CH <sub>3</sub> -O-CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> .	0		1.96e+5	0%	0%	0%	30%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-C[O.] -> CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-O-CH <sub>2</sub> -C[.] -> (CH <sub>3</sub> )-CH <sub>3</sub>	0		2.70e+4	1%	0%	0%	30%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH <sub>2</sub> -C[O.] -> CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-C[.] -> (CH <sub>3</sub> )-CH <sub>3</sub>	0		4.81e+5	87%	75%	100%	100%	ok
CH <sub>3</sub> -C[O.] -> CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-O-CH <sub>2</sub> -CH[.] -> OH	0		8.80e+4	3%	0%	0%	20%	ok
CH <sub>3</sub> -CH[O.] -> CH <sub>3</sub> -CH(OH)-O-CH <sub>2</sub> -CH[.] -> OH	0		8.80e+4	16%	0%	0%	25%	ok
CH <sub>3</sub> -CO-CH <sub>2</sub> -CH[O.] -> CH <sub>3</sub> -CH(OH)-CH <sub>2</sub> -CO-CH <sub>2</sub> .	0		2.53e+2	0%	0%	0%	10%	ok
CH <sub>3</sub> -C[O.] -> CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-O-CO-CH <sub>2</sub> .	0		6.72e+1	13%	0%	0%	25%	ok
<u>Estimates using alternative assumptions (see text)</u>								
<u>Decomposition Forming RO. (Rate constants estimated to best fit data on Table 32 [Equation (XIX)].)</u>								
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )O-CH <sub>2</sub> O. -> CH <sub>3</sub> -C[O.] -> CH <sub>3</sub> -C(CH <sub>3</sub> )CH <sub>3</sub> + HCHO	0	14.34	1.49e+4	9%	0%	0%	25%	ok
CH <sub>3</sub> -O-CH <sub>2</sub> -O-CH <sub>2</sub> O. -> CH <sub>3</sub> -O-CH <sub>2</sub> O. + HCHO	0	13.34	3.14e+4	17%	0%	16%	30%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated k (min <sup>-1</sup> )	%	Expt. Min	Fract React. Exp'd	Max	Estimation vs Experimental
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-CH[O.]-CH <sub>2</sub> -OH → CH <sub>3</sub> -CH[O.]-CH <sub>3</sub> + HCO-CH <sub>2</sub> -OH	0	12.35	6.55e+4	0%	0%	0%	15%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -OH → CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> O. + HCO-CH <sub>2</sub> -OH	0	11.55	1.19e+5	0%	0%	0%	25%	ok
Decomposition Forming RO. (Rate constants estimated to best fit data on Table 32 [Equation (XIX)].) (continued)								
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -O-CO-CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CHO	0	11.54	1.20e+5	1%	0%	0%	30%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>2</sub> -OH → CH <sub>3</sub> -CH <sub>2</sub> O. + HCO-CH <sub>2</sub> -OH	0	11.54	1.20e+5	0%	0%	0%	25%	ok
CH <sub>3</sub> -CH(OH)-CH[O.]-O-CH <sub>3</sub> → CH <sub>3</sub> O. + CH <sub>3</sub> -CH(OH)-CHO	0	11.49	1.24e+5	0%	0%	0%	15%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-CH[O.]-CH <sub>3</sub> → CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-CH <sub>3</sub> + CH <sub>3</sub> -CHO	0	11.07	1.70e+5	30%	0%	0%	20%	High: 30% vs 20%
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CO-CH <sub>3</sub> → CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> -CO <sub>2</sub> .	0	10.73	2.18e+5	100%	10%	24%	50%	High: 100% vs 50%
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]-O-CH <sub>3</sub> → CH <sub>3</sub> O. + CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CHO	0	10.34	2.92e+5	0%	0%	0%	30%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(CH <sub>3</sub> )-O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> → CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	10.29	3.03e+5	11%	0%	0%	20%	ok
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH → HO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CHO	0	10.13	3.41e+5	0%	0%	0%	25%	ok
CH <sub>3</sub> -CH(CH <sub>3</sub> )-O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> → CH <sub>3</sub> -CH[O.]-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	10.09	3.51e+5	12%	0%	0%	20%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	0	10.07	3.57e+5	47%	0%	0%	50%	ok
CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> → CH <sub>3</sub> -CO-O-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	0	10.07	3.57e+5	46%	0%	0%	25%	High: 46% vs 25%
CH <sub>3</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>2</sub> -OH → HO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	0	10.07	3.57e+5	43%	0%	0%	25%	High: 43% vs 25%
CH <sub>3</sub> -CH <sub>2</sub> -O-CH[O.]-CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CHO	0	10.06	3.59e+5	48%	0%	0%	15%	High: 48% vs 15%
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>3</sub> → CH <sub>3</sub> -CO-CH <sub>3</sub> + CH <sub>3</sub> O.	0	9.50	5.45e+5	0%	5%	13%	25%	Low: 0% vs 5%
CH <sub>3</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> → CH <sub>3</sub> -CH(CH <sub>2</sub> O.)-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	9.29	6.37e+5	20%	0%	18%	40%	ok
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>2</sub> -OH → HO-CH <sub>2</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	9.29	6.37e+5	20%	0%	0%	20%	ok
CH <sub>3</sub> -C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-C[O.](CH <sub>3</sub> )-CH <sub>3</sub> → CH <sub>3</sub> -C(OH)(CH <sub>2</sub> O.)-CH <sub>3</sub> + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	9.29	6.37e+5	20%	0%	0%	25%	ok
CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-O-CH <sub>2</sub> -CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CO-CH <sub>3</sub>	0	9.28	6.41e+5	20%	0%	31%	100%	ok
CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CH[O.]-O-CH <sub>2</sub> -CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> O. + CH <sub>3</sub> -CH <sub>2</sub> -O-CO-CH <sub>2</sub> -CHO	0	7.99	1.67e+6	2%	0%	16%	20%	ok

Table 34 (continued)

Reaction Type and Reaction	Rad. [a]	Hr (kcal)	Estimated k (min <sup>-1</sup> )	%	Expt. Fract React. Min Exp'd Max	Estimation vs Experimental
<u>Isomerizations with -O- in transition state ring (Estimates assuming no excess ring strain energy)</u>						
CH3-CH2-O-CH[O.] -CH3 -> CH3-CH(OH)O-CH2-CH2.	0		2.15e+5	29%	0% 0% 25%	High: 29% vs 25%
CH3-C(CH3)(CH3)O-CH2O. -> CH3-C(CH3)(CH2.)O-CH2-OH	0		6.46e+5	80%	0% 0% 25%	High: 80% vs 25%
CH3-C(CH3)(CH3)O-CH[O.] -CH3 -> CH3-C(CH3)(CH2.)O-CH(OH)CH3	0		6.46e+5	57%	0% 0% 20%	High: 57% vs 20%
CH3-CH(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH(CH2.)-CH3	0		4.31e+5	13%	0% 0% 20%	ok
CH3-C(CH3)(CH3)-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(CH2.)-O-C(CH3)(OH)-CH3	0		6.46e+5	18%	0% 0% 20%	ok
CH3-CH2-O-CO-CH2-CH[O.] -O-CH2-CH3 -> CH3-CH2-O-CO-CH2-CH(OH)-O-CH2-CH2.	0		2.15e+5	0%	0% 0% 20%	ok
CH3-CH2-O-CO-CH2-CH2-O-CH[O.] -CH3 -> CH3-CH(OH)-O-CH2-CH[.] -CO-O-CH2-CH3	0		9.19e+5	63%	0% 0% 50%	High: 63% vs 50%
CH3-CO-O-CH2-CH2-O-CH[O.] -CH3 -> CH3-CH(OH)-O-CH2-CH[.] -O-CO-CH3	0		1.08e+7	95%	0% 0% 25%	High: 95% vs 25%
CH3-CH2-CH2-CH[O.] -O-CH2-CH2-OH -> CH3-CH2-CH2-CH(OH)-O-CH2-CH[.] -OH	0		3.49e+7	18%	0% 0% 25%	ok
CH3-CH2-CH2-CH2-O-CH[O.] -CH2-OH -> CH3-CH2-CH[.] -CH2-O-CH(OH)-CH2-OH	0		7.26e+6	0%	0% 0% 25%	ok
CH3-CH2-CH2-CH[O.] -O-CH3 -> CH3-O-CH(OH)-CH2-CH2-CH2.	0		2.15e+5	0%	0% 0% 30%	ok
CH3-CH(CH3)-CH2-O-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-O-CH2-C[.](CH3)-CH3	0		1.06e+7	78%	0% 0% 30%	High: 78% vs 30%
CH3-CH(CH3)-O-CH2-C[O.](CH3)-CH3 -> CH3-C(CH3)(OH)-CH2-O-C[.](CH3)-CH3	0		1.89e+8	100%	75% 100% 100%	ok
CH3-C[O.](CH3)-O-CH2-CH2-OH -> CH3-C(CH3)(OH)-O-CH2-CH[.] -OH	0		3.49e+7	92%	0% 0% 20%	High: 92% vs 20%
CH3-CH[O.] -O-CH2-CH2-OH -> CH3-CH(OH)-O-CH2-CH[.] -OH	0		3.49e+7	99%	0% 0% 25%	High: 99% vs 25%
CH3-CO-CH2-CH[O.] -CH3 -> CH3-CH(OH)-CH2-CO-CH2.	41		9.32e+4	47%	0% 0% 10%	High: 47% vs 10%

[a] Radical number on Table 33



Based on the approach used by Atkinson (1996), the activation energies for the decomposition reactions are estimated assuming

$$E_a(\text{decomposition}) = E_{aA} + E_{aB} \cdot \Delta H_r \quad (\text{XIV})$$

where  $E_{aA}$  and  $E_{aB}$  are parameters which are assumed to depend only on the type of radical which is formed in the decomposition. The derivation of these parameters for the various types of decomposition reactions is discussed below.

We will first consider decompositions forming methyl radicals, for which, as shown on Table 32, there are the most extensive and best characterized data. These come in two groups: decompositions of hydrocarbon alkoxy radicals (i.e., alkoxy radicals containing only  $-\text{CH}_3$ ,  $-\text{CH}_2-$ ,  $>\text{CH}-$ , or  $>\text{C}<$  groups) which tend to be endothermic by  $\sim 5$  to  $\sim 13$  kcal/mole and relatively slow, and decompositions of alkoxy radicals with  $\alpha$ -O groups such as formed in photooxidations of ethers, which are exothermic by  $\sim 5$  kcal/mole and tend to be much more rapid. Note that the rate constants for the latter are uncertain because of uncertainty in the estimates for the  $\text{O}_2$  reaction used to place the experimental rate constant ratio on an absolute basis. It is possible that the  $\text{O}_2$  reaction is significantly faster than estimated in this work, in which case these decompositions will also be faster.

Figure 8 shows plots of the estimated activation energy for selected decompositions reactions vs. the estimated heats of reaction. It can be seen that the data for reactions forming methyl radicals fall reasonably well on a straight line, if the point for the 2-methyl-2-butoxy radical, which seems to be somewhat inconsistent with the other data, is excluded. The least squares line (excluding the point for 2-methyl-2-butoxy) is

$$E_a(\text{decomp. to } \text{CH}_3) = 14.05 + 0.44 \Delta H_r \quad (\text{XV})$$

where  $E_a$  is the activation energy and  $\Delta H_r$  is the estimated heat of reaction, both in kcal/mole. This corresponds to  $E_{aA} = 14.05$  kcal/mole and  $E_{aB} = 0.44$ . These are used for estimating activation energies for all the alkoxy radical decompositions forming methyl radicals.

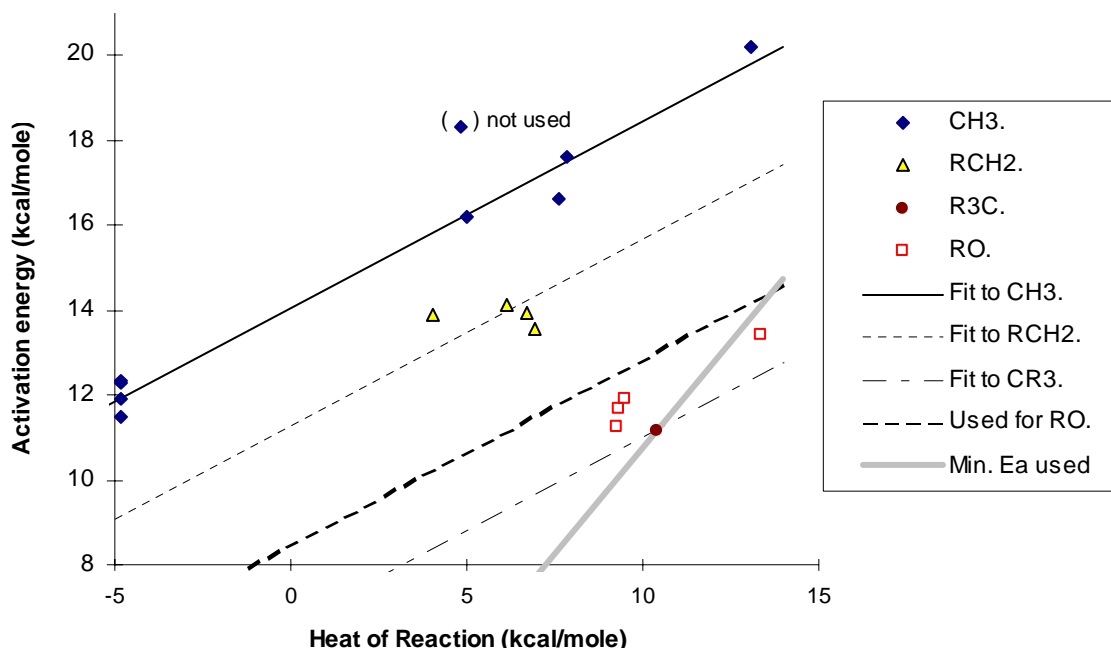


Figure 8. Plots of estimated or measured activation energies vs. heats of reaction for various alkoxy radical decompositions.

Figure 8 shows that Equation (XV) overpredicts the activation energies for reactions forming ethyl and propyl radicals. However, the data for these decompositions are reasonably well fit if EaB is assumed to be the same as for reactions forming methyl radicals, and EaA is reduced to 11.25 kcal/mole, i.e.,

$$E_a(\text{decomp. to RCH}_2\cdot) = 11.25 + 0.44 \Delta H_r \quad (\text{XVI})$$

Although the data are not sufficient to determine whether the EaB for decompositions forming these radicals is necessarily the same as for those forming methyl, this is assumed for lack of sufficient data to determine otherwise. Likewise, the single measurement for a decomposition forming tertiary radicals is fit using EaA = 6.58 kcal/mole, and the least uncertain measurement for a decomposition forming HOCH<sub>2</sub>· is fit using EaA = 7.42 kcal/mole, if it is assumed that the same EaB is applicable for reactions assuming these radicals as well. Thus,

$$E_a(\text{decomp. to R}_3\text{C}\cdot) = 6.58 + 0.44 \Delta H_r \quad (\text{XVII})$$

$$E_a(\text{decomp. to HOCH}_2\cdot) = 7.43 + 0.44 \Delta H_r \quad (\text{XVIII})$$

can be used to estimate activation energies for these types of decompositions.

Quantitative information concerning decompositions forming alkoxy radicals is sparse, though as shown on Table 33 and Table 34 there are a number of cases where upper or lower limit estimates can be obtained. As shown on Table 32, there is only one system where information on the rate relative to a competing O<sub>2</sub> reaction is available, but the information concerns a minor reaction route and the rate constant ratio must be considered to be highly uncertain (see Table 33). The only other

quantitative information concerns two radicals where decomposition to an alkoxy radical competes with a decomposition forming a methyl radical. If equation (XIII) and (XV) are used to estimate the Arrhenius parameters and thus the rate constants for these competing decompositions to methyl radicals, then the rate constants forming alkoxy radicals can be placed on an absolute basis. If this is assumed, and if the same EaB is used as assumed for the reactions forming alkyl or HOCH<sub>2</sub>· radicals, then a value of EaA = 7.42 kcal/mole can be derived, i.e.,

$$E_a (\text{decomp to RO} \cdot - \text{initial estimate}) = 7.50 + 0.44 \Delta H_r \quad (\text{XIX})$$

Note that using Equation (XIX) gives a reasonably good fit to the data for the decomposition determined relative to the O<sub>2</sub> reaction, even though this was not used in its derivation.

However, although use of Equation (XIX) to predict alkoxy-forming decomposition activation energies gives good fits to the limited quantitative product yield data, Table 34 shows that there are many cases where it results in predictions which are inconsistent with upper limit data concerning the relative importance of this reaction (see “rate constants estimated to best fit data on Table 32” in the “alternative assumptions” section of the table). Therefore, use of Equation (XIX) appears to be biased towards overpredicting the relative importance of this reaction. Such a bias is not acceptable as a basis for deriving a general methodology for deriving estimated VOC reaction mechanisms, and if uniformly good predictions cannot be obtained, at a minimum the prediction method should be as likely to underpredict as overpredict.

To obtain unbiased estimates for the relative importances of these decompositions, an optimization was performed to minimize the cases where the estimates were outside of the estimated upper and lower limit ranges, as well as to minimize the discrepancies between estimated and experimental quantitative yield ratios. This optimization was done in two ways: one where EaA was adjusted and EaB was held fixed at the 0.44 value as assumed for the reactions forming alkyl radicals, and the other where both EaA and EaB were optimized. However, the qualities of the fits were not significantly different in either case, so for consistency with the estimates for the other reactions we will only use the data where we assumed EaB = 0.44. The results of this optimization yielded EaA = 8.44 kcal/mole, i.e.,

$$E_a (\text{decomp to RO} \cdot - \text{recommended}) = 8.43 + 0.44 \Delta H_r \quad (\text{XX})$$

This resulted in overpredicting the apparent activation energies for the three alkoxy-forming decompositions on Table 32 by ~1 kcal/mole each, which corresponds to an underprediction of the 298K rate constant by a factor of ~6. However, use of Equation (XX) for predicting activation energies for alkoxy-forming decompositions is preferred over Equation (XIX) because the latter removes the apparent bias towards overpredicting upper limit rate constants. In particular, this gives only two cases (as opposed to 5 for Equation XIX) where the prediction is outside the estimation is outside the estimated uncertainty range of the experimental data.

The estimates discussed above do not cover all the types of radicals that may be formed in alkoxy radical decompositions, and methods are needed to estimate EaA values for cases where there are no data. Atkinson (1997b) observed that there is an apparent correlation between the EaA and the ionization potential of the radical formed, and used this to derive a general estimation method for all alkoxy radical decompositions. Plots of the EaA values obtained as discussed above against ionization potential of the radical formed is shown on Figure 9. The IP's used are given in Table 35 and are from the NIST (1994) database. It can be seen that the three points for the alkyl (methyl, ethyl, propyl and t-butyl) radicals are reasonably well fit by a straight line, which is given by

$$E_{aA} \text{ (decomp. to hydrocarbon radicals)} = -8.73 + 2.35 \text{ IP} \quad (\text{XXI})$$

where  $E_{aA}$  is in kcal/mole and IP is the ionization potential of the radical formed in eV. When combined with Equation (XIV), and using  $E_{aB} = 0.44$  as discussed above, this yields

$$E_a \text{ (decomp. to hydrocarbon radicals)} = -8.73 + 2.35 \text{ IP} + 0.44 \Delta H_r \quad (\text{XXII})$$

where IP is in eV and  $E_a$  and  $\Delta H_r$  is in kcal/mole. This is close to the general relationship derived by Atkinson (1997a), which is

$$E_a \text{ (general decompositions)} = -8.1 + 2.4 \text{ IP} + 0.36 \Delta H_r. \quad (\text{XXIII})$$

The small differences between these equations are due to the fact that in this work the  $E_{aB}$  parameter is determined using only the reactions forming methyl radicals, and that Atkinson (1996) did not include the exothermic decompositions of the radicals from the ether systems in his analysis, but did include the reaction forming  $\text{HOCH}_2\cdot$ .

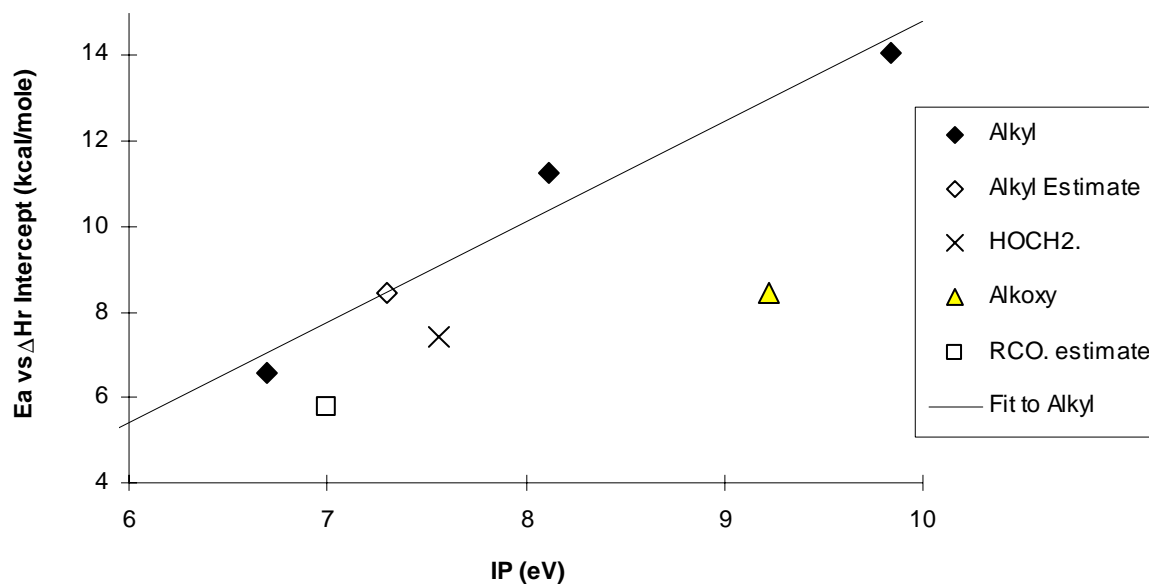


Figure 9. Plots of intercepts of lines used to predict activation energies from heats of reactions for various types of alkoxy radical decompositions vs. the ionization potential of the radical formed. These are based on assuming all lines have the same slope as fits the data for reactions forming methyl radicals.

Table 35. Summary of ionization potentials and EaA parameters used to estimate activation energies for alkoxy radical decompositions from the heats of reactions.

Type of radical Formed [a]	IP [b] (eV)	EaA (kcal/mole)	Derivation of EaA
CH <sub>3</sub> .	9.84	14.05	Derived from least squares fits of Ea vs Hr as discussed in the text (Equation (XV)). The EaB derived from these data are assumed to be applicable for all alkoxy radical decompositions.
RCH <sub>2</sub> .	8.12	11.25	Derived to by adjusting EaA to fit the data as discussed in the text (Equation (XVI)).
RCH[.]R	7.30	8.46	EaA is estimated from the IP using Equation (XXI). See text.
R <sub>2</sub> C[.]R	6.70	6.58	Derived to by adjusting EaA to fit the data as discussed in the text (Equation (XVII)).
RO.	9.22	8.43	Derived to minimize errors and biases in predictions of relative product yield data as discussed in the text (Equation XX).
OH	13.00	8.43	EaA assumed to be the same as derived for decompositions forming alkoxy radicals. This is highly uncertain.
HCO.	~8.8? [c]	9.99	Estimated from the IP using Equation (XXI), with the intercept reduced by 2.0 kcal/mole to give predictions which are more consistent with the limited available upper and lower limit data. Highly uncertain and may be upper limit.
R'C(O).	7.00	5.76	(see above)
R'C(O)O.		12.00	Necessary to assume that decompositions forming RCO <sub>2</sub> . radicals is slow to be consistent with product data from reaction of OH with isopropyl and t-butyl acetates, and for model simulations to fit chamber data for propylene carbonate. The EaA value used is the lowest value that is consistent with the data for propylene carbonate.
HOCH <sub>2</sub> .	7.56	7.43	Derived to by adjusting EaA to fit the data as discussed in the text (Equation (XVIII)).
RCH[.]OH	6.70	5.41	Estimated from the IP using Equation (XXI), with the intercept reduced by 1.65 kcal/mole to correctly predict the data for the decomposition of HOCH <sub>2</sub> CH <sub>2</sub> O. to HOCH <sub>2</sub> .
R <sub>2</sub> C[.]OH		4.21	Ratio of EaA for R <sub>2</sub> C[.]OH to R <sub>2</sub> C[.]R assumed to be the same as ratio of EaA's for RCH[.]OH to RCH[.]R.
R'OCH <sub>2</sub> .	6.94	11.25	Better fits to available data are obtained if reactions forming ROCH <sub>2</sub> . Radicals have the same activation energies as those forming RCH <sub>2</sub> radicals.
RCH[.]OR'		7.46	R'O- substitution assumed to reduce EaA by 1 kcal/mole relative to alkyl substitution to fit data for a minor product from isopropyl acetate. This is highly uncertain, and the data are also consistent with reducing EaA even further.
R <sub>2</sub> C[.]OR'		5.58	R'O- substitution assumed to reduce EaA by 1 kcal/mole to be consistent with assumption made when estimating EaA for RCH[.]OR'. This is highly uncertain.
ROC(O).		12.00	Derived to be such that this decomposition is predicted to be minor for CH <sub>3</sub> -O-CO-CH <sub>2</sub> -CH[O.]CO-O-CH <sub>3</sub> radicals, but is the dominant process for CH <sub>3</sub> -C[O.](CH <sub>3</sub> )-CO-O-CH <sub>3</sub> , for model predictions to be consistent with environmental chamber reactivity data for dimethyl succinate (DBE-4) and methyl isobutyrate, respectively.
XC(O)CH <sub>2</sub> .		11.25	For lack of available data, R'C(O)- and HC(O)- substitution is assumed to have no effect on EaA.
RCH[.]C(O)X		8.46	(see above)
R <sub>2</sub> C[.]C(O)X		6.58	(see above)

[a] "R" is any substituent where the radical center is bonded to a non-carbonyl carbon. "R'" is any substituent other than H. "X" is any substituent, including H.

[b] IP data from NIST (1994) and is given for the methyl substituted species except where indicated.

[c] Not in NIST database. Entry of "8.8?" given in Lange's handbook of chemistry (1985).

Figure 9 shows that Equation (XXI) overpredicts the EaA for the reaction forming  $\text{HOCH}_2\cdot$  by 1.65 kcal/mole, resulting in an underprediction of the 298K rate constant by a factor of ~16. However, it can be argued that the discrepancy is not large considering the data and the assumptions behind the empirical correlations. Equation (XXI) clearly fails in the case of reactions forming alkoxy radicals, overpredicting activation energies by over 4.5 kcal/mole and the decomposition rate constants by three orders of magnitude. For that reason, we conclude that Equations (XXI) should only be used for reactions forming carbon-centered radicals. For substituted radicals the actual data should be used to derive EaA estimates whenever possible.

Based on these considerations, together with the availability of IP data, Equation (XXI) can therefore be used to derive the EaA parameters for decompositions forming secondary alkyl radicals ( $\text{R}_2\text{CH}\cdot$ ), and a modified version of Equation (XXI), where the EaA is reduced by 1.65 kcal/mole so its predictions are consistent with the data for the reaction forming  $\text{HOCH}_2\text{O}\cdot$ , can be used to estimate EaA for reactions forming  $\text{CH}_3\text{C}(\cdot)\text{OH}$ . In the case of reactions forming  $\text{HCO}$  and  $\text{RC}(\text{O})\cdot$  radicals, predictions that are reasonably consistent with the limited upper and lower limit data (see Table 34) if the EaA predicted using Equation (XXI) is reduced by ~2 kcal/mole. These estimates are given on Table 35, together with the EaA values derived for the decompositions discussed above, and the associated ionization potentials. Obviously, these EaA estimates are the least uncertain for secondary alkyl radicals, are highly uncertain for formyl and acetyl radicals.

Available IP data and Equation (XXI) (or the modified version of it) can also be used to derive an EaA for reactions forming  $\text{CH}_3\text{OCH}_2\cdot$  radicals, which presumably could also be applied to reactions forming other radicals of the type  $\text{ROCH}_2\cdot$ . However, applying this approach to reactions forming these radicals predict that this type of reaction is extremely rapid (having rate constants  $> 10^9 \text{ sec}^{-1}$ ) in at least two cases where available data are inconsistent with this reaction dominating (see Table 34 and radicals 19 and 31 on Table 33). Predictions are more consistent with the data if the activation energies are derived assuming the same EaA as employed for reactions forming alkyl  $\text{RCH}_2\cdot$  radicals. For other radicals, Equation (XII) is either not applicable or cannot be used because of lack of available IP data.

For reactions forming substituted alkyl radicals (i.e., reactions forming radicals with non-alkyl substituents) we assume that  $\beta$ - or further substituents on the radical formed have no effect, and make various estimates concerning the effects of various types of  $\alpha$ -substituents, based on highly uncertain assumptions or fits to a very limited data base. In several cases, adjustments were made so the predictions would be consistent with product data or with environmental chamber reactivity data for several compounds. For example, it was initially assumed that decompositions forming  $\text{RC}(\text{O})\text{O}\cdot$  radicals have the same parameters as those forming simple alkoxy ( $\text{RO}\cdot$ ) radicals, but,, as indicated on Table 35, this better fits to product and environmental chamber data for several compounds were obtained if a much higher EaA value was used. These estimates, which are obviously very uncertain, are summarized on Table 35.

Although this is not the case with any of the radicals listed on Table 33, there may be cases where Equation (XIV) and the recommended EaA and EaB values may predict unreasonably low or negative activation energies. For general estimation purposes, we assume a minimum decomposition energy of ~0.75 kcal/mole. Thus if Equation (XIV) predicts a lower activation energy lower than that, then 0.75 kcal/mole is used. Although the possibility of a lower minimum cannot be ruled out, the data for the decomposition of neopentoxo and  $\text{HOCH}_2\text{CH}_2\text{O}\cdot$  radicals tend to rule out the minimum being higher than this.

The above discussion, based on the use of Equation (XIV), all incorporate the assumption that the activation energy for the decomposition only depends on the nature of the radical formed and the overall heat of reaction. With appropriate choices of EaA, as shown on Table 35, this gives predictions which, though not always consistent with the data to within the experimental uncertainty, are at least good to within an order of magnitude in most cases. Note that this assumption implies that the activation energy does not depend on the nature of the carbonyl compound that is formed. This appears to work in the case of reactions forming aldehydes, ketones, or esters, which is the case for most of the reactions listed on Table 33.

However, this assumption appears to fail in the case of reactions where the carbonyl group formed is in an anhydride or carbonate anhydride, i.e., is contained in a -C(O)OC(O)- structure. The data of Tuazon et al (1989b) indicate that the  $\text{CH}_3\text{C}[\text{O}](\text{CH}_3)\text{OC}(\text{O})\text{CH}_3$  radical formed in the reactions of OH radicals with t-butyl and isopropyl acetates (radical 40 on Table 33) decomposes to a significant extent to form acetic anhydride and methyl radicals, while Equation (XIV) and the parameters that fit the data for most of the other methyl radical-forming reactions predict that this reaction is sufficiently slow that the competing isomerization pathway, which is not observed, would dominate<sup>12</sup>. In addition, reactivity and product data recently obtained from a carbonate compound can only be explained if an analogous reaction of a carbonate-containing radical is much more rapid than predicted by these estimates (unpublished results from this laboratory). The data of Tuazon et al (1998b), together with the estimated rate constant for the competing decomposition of  $\text{CH}_3\text{C}[\text{O}](\text{CH}_3)\text{OC}(\text{O})\text{CH}_3$  to acetone and  $\text{CH}_3\text{CO}_2\cdot$ , can be predicted if the reactions forming anhydride products have a 2 kcal/mole lower reaction energy than predicted using Equation (XIV), and other data from our laboratory are also better fit if this is assumed.

Therefore, for estimating activation energies for  $\beta$ -scission decompositions that form carbonyl compounds with -C(O)OC(O)- structures, the following modified version of Equation (XIV) is employed:

$$E_a(\text{decomposition forming } R\cdot + \text{-CO-O-CO-}) = E_{aA} + E_{aB} \cdot \Delta H_r - 2 \text{ kcal/mole} \quad (\text{XXIV})$$

Where EaA is derived based on the radical, R·, that is formed as shown on Table 35, and the same EaB value is used as assumed for all other reactions. This is obviously uncertain because it is derived based on highly uncertain estimates for competing rate constants (see radical 40 on Table 33), and is based on only a limited number of reactions. However, employing this correction means that the mechanism estimation system gives branching ratio predictions that are consistent with the limited data that are currently available.

The decomposition activation energy and rate constant estimates discussed in this section are obviously highly uncertain in many (if not most) cases, being based in many cases on very uncertain alkoxy + O<sub>2</sub> rate constants, employing many highly uncertain and untested assumptions, and not giving satisfactory predictions in all cases. Clearly, additional data are needed, particularly for reactions of oxygen-containing alkoxy radicals, to test, refine, and improve these estimates and the many assumptions they incorporate. Indeed, it may not be possible to develop a totally satisfactory estimation method that can accurately predict rate constants for the full variety of these reactions, without carrying out detailed theoretical calculations for each system. Thus, rate constants or branching ratios derived from experimental data should always be used whenever possible when developing reaction mechanisms for

<sup>12</sup> The decomposition is predicted to dominate even after the ring strain correction of 3.5 kcal/mole for transition states containing -O- or -CO- groups is added, as discussed in Section II.B.10.d.



atmospheric reactivity predictions. However, when no data are available, we have no choice but to use estimates such as those discussed in this section.

#### d. Isomerization Corrections

As discussed above, when estimating alkoxy radical isomerization rate constants, an additional 3.5 kcal/mole is added to the activation energy if the cyclic transition state contains -O-, -C(O)- or -OC(O)- groups. The need for this correction is shown on Table 34, which compares the experimental and predicted upper and lower limit branching ratios for these isomerizations with and without this correction. It can be seen that if the additional 3.5 kcal/mole is not added to the activation energy, there are 8 cases where isomerization is predicted to be important where the experimental data indicate it is not. This overprediction of the importance of isomerization is removed when the additional 3.5 kcal/mole activation energy is assumed. On the other hand, if a strain energy of greater than that is assumed, then the estimation becomes inconsistent with the observation that the  $\text{CH}_3\text{CH}(\text{CH}_3)\text{-OCH}_2\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_3$  reacts primarily by isomerization (Stemmler et al, 1997a).

Note that if it is assumed that the reactions of  $\text{O}_2$  with the O-substituted alkoxy radicals are much more rapid than estimated in this work, as predicted, for example, by the estimation method of Atkinson (1997a), then many of the competing decompositions would also be predicted to be faster, and this isomerization strain correction may not be necessary. Obviously this isomerization correction, as well as all our estimates concerning the decomposition reactions, would need to be revisited if new data indicate that our estimates concerning these alkoxy +  $\text{O}_2$  reactions are incorrect.

#### e. Ester Rearrangement

Tuazon et al (1998b) recently reported data indicating that  $\alpha$ -ester-substituted alkoxy radicals undergo a second type of hydrogen shift isomerization, where the hydrogen  $\alpha$  to the alkoxy center shifts, via a 5-member ring transition state, to the ester carbonyl oxygen atom, forming an acid and an acyl radical, e.g.,



In the case of the alkoxy radical formed from ethyl acetate [ $\text{CH}_3\text{CH}(\text{O}\cdot)\text{O-CO-CH}_3$ ], this reaction dominates over the competing reactions of this alkoxy radical (primarily reaction with  $\text{O}_2$  and decomposition to  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CO}_2\cdot$ ), which are estimated to have a total rate constant of  $\sim 5 \times 10^4 \text{ sec}^{-1}$  under atmospheric conditions. This means that these “ester rearrangements” must react with a rate constant of at least  $\sim 3 \times 10^5 \text{ sec}^{-1}$  under these conditions. Obviously provisions for these reactions need to be included in the mechanism estimation and generation system.

There is no information available upon which to base quantitative estimates for the rate constant for this reaction, other than the fact that the rate constant for  $\text{CH}_3\text{CH}(\text{O}\cdot)\text{O-CO-CH}_3$  radicals is at least  $\sim 3 \times 10^5 \text{ sec}^{-1}$ , assuming the estimates for the competing reactions of this radical are correct. However, if the reaction is assumed to be much faster than this, then significant yields of PAN precursors are predicted to be formed in the photooxidation of n-butyl acetate, and models assuming this give predictions that are not consistent with results of environmental chamber experiments with this compound (Carter et al, 1999a). The PAN precursor  $\text{CH}_3\text{C}(\text{O})\cdot$  would result from the ester rearrangement of the  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{O-CO-CH}_3$  radical, which competes with the 1,4-H shift isomerization to  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{O-CO-CH}_3$ , which has an estimated rate constant of  $2 \times 10^5 \text{ sec}^{-1}$ . To minimize this apparent inconsistency, we assume that all ester rearrangements occur with the estimated lower limit rate constant of  $3 \times 10^5 \text{ sec}^{-1}$ .

To obtain a rough estimate of temperature dependence, we assume that these ester rearrangements have an A factor which is approximately the same as that used for 1,4-H shift isomerizations, based on expected similarities in the structure of the transition states. If a T=298K rate constant of  $3 \times 10^5 \text{ sec}^{-1}$  is assumed, this corresponds to

$$k(\text{ester rearrangement}) \approx 8 \times 10^{10} e^{-3723/T} \text{ sec}^{-1} \quad (\text{XXV})$$

Obviously, this is highly uncertain, and quantitative information concerning relative rates of competing reactions involving this rearrangement, or at least more upper or lower limit data, would significantly reduce the uncertainty of these estimates.

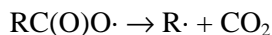
Tuazon et al (1998b) saw no evidence that the analogous ester rearrangement reaction involving a 6-member ring transition state that might be expected to occur in the t-butyl acetate system, e.g.,



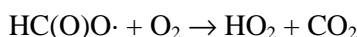
in fact occurs to any significant extent. Of course, this could be because the competing decomposition to  $\text{HCHO} + \text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{-O-CO-CH}_3$  is predicted to be very fast, with an estimated rate constant of  $\sim 3 \times 10^7 \text{ sec}^{-1}$ . Nevertheless, we tentatively assume that these reactions are not important, and the possibility that they may occur is not presently incorporated in the mechanism generation system. However, the possibility that this occurs needs to be investigated.

#### f. Acyloxy Radicals

Acyloxy radicals are radicals of the form  $\text{RC(O)O}\cdot$  or  $\text{HC(O)O}\cdot$ . It is expected that the decomposition of  $\text{RC(O)O}\cdot$  to  $\text{R}\cdot$  and  $\text{CO}_2$ ,



should be rapid, based on thermochemical considerations, so this is assumed to be its major fate when it is generated in the mechanisms. In the case of  $\text{HC(O)O}\cdot$ , it is assumed to be consumed by rapid reaction with  $\text{O}_2$ .



Although it is also possible that it may primarily decompose to  $\text{H}\cdot + \text{CO}_2$ , under atmospheric conditions the net effect would be the same because the major fate of  $\text{H}\cdot$  atoms is reaction with  $\text{O}_2$ , forming  $\text{HO}_2$ .

#### g. Explicit Alkoxy Reaction Assignments

Because of the uncertainties in estimating alkoxy radical rate constants, explicit assignments of alkoxy radical rate constants or branching ratios are used rather than estimates whenever there are sufficient data available to make such assignments. These are shown on Table 30 through Table 33, above, where Table 30 contains the explicit assignments for the three measured alkoxy +  $\text{O}_2$  reactions, Table 31 shows the assignments used for the butoxy and pentoxy isomerizations, Table 32 shows the assignments for those decompositions where quantitative rate constant assignments could be made, and Table 33 shows the assignments where the available data are appropriate for assigning branching ratios only. Note that many of these are quite uncertain, in most cases being based on highly indirect determinations or adjustments in complex mechanisms to fit reactivity data in chamber experiments, and having highly uncertain, usually estimated, reference rate constants. Note also that the system does not

incorporate temperature dependence estimates for those reactions on Table 33 where only branching ratio assignments could be made, so the estimates may not be applicable for temperatures much different from ~300K. Nevertheless, these are less uncertain than the rate constants or branching ratios that have to be based entirely on estimates.

The reactions of isoprene, isoprene products and alkynes involve the formation of radicals whose mechanisms cannot be estimated because of lack of available thermochemical data, so explicit assignments have to be made in those cases so reactions of those compounds could be generated. These assignments are listed on Table 36, along with footnotes indicating the basis for the assignments. Note that those for radicals formed from isoprene and its products are based on estimates incorporated in the isoprene and isoprene products mechanism of Carter and Atkinson (1996), and those for other radicals are based on analogy for reactions of similar radicals for which estimates could be made.

Table 36. Explicit assignments for reactions of alkoxy radicals whose mechanisms could not be estimated.

Radical	Products	Ratio	Notes
<u>Isoprene Intermediates</u>			
HO-CH <sub>2</sub> -C(CH <sub>3</sub> )=CH-CH <sub>2</sub> O.	HO-CH <sub>2</sub> -CH=C(CH <sub>3</sub> )-CH[.] -OH		1
HO-CH <sub>2</sub> -C(CH <sub>3</sub> )=CH(CH <sub>2</sub> O.)	HO-CH <sub>2</sub> -C(CH <sub>2</sub> .)=CH(CH <sub>2</sub> -OH)		1
CH <sub>2</sub> =C(CH <sub>2</sub> -OH)-CH[O.] -CH <sub>2</sub> -OH	CH <sub>2</sub> =C(CHO)-CH <sub>2</sub> -OH + HO-CH <sub>2</sub> .		1
CH <sub>2</sub> =CH-C[O.](CH <sub>3</sub> )-CH <sub>2</sub> -OH	CH <sub>2</sub> =CH-CO-CH <sub>3</sub> + HO-CH <sub>2</sub> .		1
CH <sub>3</sub> -C(CH <sub>2</sub> O.)=CH(CH <sub>2</sub> -OH)	HO-CH <sub>2</sub> -C(CH <sub>3</sub> )=CH-CH[.] -OH		1
CH <sub>3</sub> -C(CH <sub>2</sub> O.)=CH-CH <sub>2</sub> -OH	CH <sub>3</sub> -C(CHO)=CH-CH <sub>2</sub> -OH + HO <sub>2</sub> .		1
CH <sub>2</sub> =C(CH <sub>3</sub> )-CH[O.] -CH <sub>2</sub> -OH	CH <sub>2</sub> =C(CHO)-CH <sub>3</sub> + HO-CH <sub>2</sub> .		1
CH <sub>2</sub> =CH-C(OH)(CH <sub>2</sub> O.)-CH <sub>3</sub>	*C(CH <sub>3</sub> )(OH)-CH <sub>2</sub> -O-CH <sub>2</sub> -CH[.] -*		1
CH <sub>2</sub> =C(CH <sub>3</sub> )-CH(CH <sub>2</sub> O.)-OH	*CH(OH)-C[.](CH <sub>3</sub> )-CH <sub>2</sub> -O-CH <sub>2</sub> -*		1
CH <sub>2</sub> =CH-CO-CH <sub>2</sub> O.	HCHO + CH <sub>2</sub> =CH-CO.		1
<u>Isoprene Product Intermediates</u>			
HCO-CO-CH <sub>2</sub> O.	HCHO + HCO-CO.		1
.OCH <sub>2</sub> -CH=C(CH <sub>3</sub> )-CH <sub>2</sub> -ONO <sub>2</sub>	HCO-CH=C(CH <sub>3</sub> )-CH <sub>2</sub> -ONO <sub>2</sub> + HO <sub>2</sub> .	80%	1
	HO-CH <sub>2</sub> -CH=C(CH <sub>3</sub> )-CH[.] -ONO <sub>2</sub>	20%	
<u>Alkyne and Diene Intermediates</u>			
CH <sub>3</sub> -CH[O.] -CO-CHO	CH <sub>3</sub> -CHO + HCO-CO.		2
CH <sub>3</sub> -CO-CO-CH <sub>2</sub> O.	HCHO + CH <sub>3</sub> -CO-CO.		3
CH <sub>2</sub> =CH-CH[O.] -CH <sub>2</sub> -OH	CH <sub>2</sub> =CH-CHO + HO-CH <sub>2</sub> .		4
HO-CH <sub>2</sub> -CH=CH(CH <sub>2</sub> O.)	HCO-CH=CH(CH <sub>2</sub> -OH) + HO <sub>2</sub> .		5
HO-CH <sub>2</sub> -CH=CH-CH <sub>2</sub> O.	HO-CH <sub>2</sub> -CH=CH-CH[.] -OH		6
CH <sub>2</sub> =CH-CH[O.] -CHO	CH <sub>2</sub> =CH-CHO + HCO.		7
.OCH <sub>2</sub> -CH=CH(CH <sub>2</sub> -ONO <sub>2</sub> )	HCO-CH=CH(CH <sub>2</sub> -ONO <sub>2</sub> ) + HO <sub>2</sub> .		5
.OCH <sub>2</sub> -CH=CH-CH <sub>2</sub> -ONO <sub>2</sub>	HO-CH <sub>2</sub> -CH=CH-CH[.] -ONO <sub>2</sub>		6
CH <sub>2</sub> =CH-CH[O.] -CH <sub>2</sub> -ONO <sub>2</sub>	CH <sub>2</sub> =CH-CO-CH <sub>2</sub> -ONO <sub>2</sub> + HO <sub>2</sub> .		8

Notes

- 1 As assumed by Carter and Atkinson (1996).
- 2 Assumed to be fast by analogy with estimated reactions for CH<sub>3</sub>-CH[O.] -CO-R radicals.
- 3 Assumed to be fast by analogy with estimated reactions for CH<sub>3</sub>-CO-CH<sub>2</sub>O. radicals.
- 4 Assumed to be fast by analogy with estimated reactions for R-CH[O.] -CH<sub>2</sub>-OH radicals.
- 5 Assumed to be fast based on lack of facile decomposition routes, and the fact that isomerization would involve a trans cyclic transition state.
- 6 Isomerization, which is permitted by the cis configuration, is expected to dominate.
- 7 Assumed to be fast by analogy with estimated reactions for R-CH[O.] -CHO radicals.
- 8 Reaction with O<sub>2</sub> estimated to be the major route based on the estimated mechanism for CH<sub>3</sub>-CH<sub>2</sub>-CH[O.] -CH<sub>2</sub>-ONO<sub>2</sub>.

#### **h. Thermochemical Assignments Used in Estimates**

Many of the estimates of alkoxy radical rate constants discussed above require a knowledge or estimate of the heats of reaction for the reactions being considered. These are estimated using the group additivity methods of Benson (1976), using updated group additivity data that were obtained primarily from the NIST (1994) thermochemical database. Although that database is extensive, it is not sufficient for many of the reactions that need to be considered, and assignments or estimates for additional groups had to be added. Table 37 and Table 38 give a complete listing of the thermochemical group assignments currently incorporated in the database. Table 37 gives the data obtained from the NIST (1994) database, and Table 38 gives the thermochemical assignments that were added for this work, indicating the source of the assignments.

Table 37. Thermochemical group assignments used for estimating heats of reaction for rate constant estimation purposes that were obtained from the NIST (1994) database, or assigned as zero. Estimation methods and notation based on Benson (1976).

Group	kcal/mole	Group	kcal/mole	Group	kcal/mole
<u>From NIST (1994)</u>					
C*_(C)	39.10	C_(C)(C*)(C)(C)	1.50	Cd_(Cd)(Cd)	6.78
C*_(C)(C)	40.95	C_(C)(Cd)	-4.76	Cd_(Cd)(Cd)(Cd)	4.60
C*_(C)(C)(C)	42.60	C_(C)(Cd)(O)	-6.50	Cd_(Cd)(Cd)(O)	8.90
C*_(C)(O)	35.10	C_(C)(Cl)	-15.60	Cd_(Cd)(CO)	5.00
C*_(CO)	37.90	C_(C)(Cl)(Cl)	-18.90	Cd_(Cd)(CO)(O)	11.60
C@_(C)(Cl)	28.40	C_(C)(Cl)(Cl)(Cl)	-24.90	Cd_(Cd)(O)	8.60
C_(*CO)	-5.40	C_(C)(Cl)(F)(F)	-106.30	CO_(C)	-29.10
C_(*CO)(C)	-0.30	C_(C)(Cl)(O)	-21.60	CO_(C)(C)	-31.40
C_(*CO)(C)(C)	2.60	C_(C)(CO)	-5.20	CO_(C)(C*)	-31.40
C_(Br)(Br)(Br)(C)	3.90	C_(C)(CO)(Cl)	-22.00	CO_(C)(Cl)	-47.92
C_(Br)(C)	-5.40	C_(C)(F)	-51.50	CO_(C)(CO)	-29.20
C_(Br)(C)(C)	-3.40	C_(C)(F)(F)	-102.30	CO_(C)(F)	-95.50
C_(Br)(C)(C)(C)	-0.40	C_(C)(F)(F)(F)	-158.00	CO_(C)(I)	-20.00
C_(Br)(C)(Cl)	-10.10	C_(C)(I)	8.00	CO_(C)(O)	-35.10
C_(C)	-10.20	C_(C)(I)(I)	26.00	CO_(Cd)	-29.10
C_(C)(C)	-4.93	C_(C)(NO2)	-14.40	CO_(Cd)(O)	-32.00
C_(C)(C)(C)	-1.90	C_(C)(O)	-8.10	CO_(Cl)(O)	-49.20
C_(C)(C)(C)(C)	0.50	C_(C)(O)(O)	-16.30	CO_(CO)	-25.30
C_(C)(C)(C)(Cd)	1.68	C_(C)(O)(O)(O)	-29.60	CO_(CO)(Cl)	-40.15
C_(C)(C)(C)(Cl)	-12.80	C_(C)(O*)	6.10	CO_(CO)(O)	-29.30
C_(C)(C)(C)(CO)	1.40	C_(C)(O*)	6.10	CO_(O)	-32.10
C_(C)(C)(C)(F)	-48.50	C_(C*)	-10.08	CO_(O)(O)	-29.70
C_(C)(C)(C)(I)	13.00	C_(Cd)	-10.20	N_(C)(F)(F)	-7.80
C_(C)(C)(C)(NO2)	-11.70	C_(Cd)(Cd)	-4.29	O_(C)	-37.90
C_(C)(C)(C)(O)	-6.60	C_(Cd)(CO)	-3.80	O_(C)(C)	-23.20
C_(C)(C)(C)(O*)	8.60	C_(CO)	-10.20	O_(C)(C*)	-23.20
C_(C)(C)(Cd)	-1.48	C_(CO)(Cl)	-10.20	O_(C)(Cd)	-30.50
C_(C)(C)(Cl)	-14.80	C_(CO)(Cl)(Cl)	-12.00	O_(C)(CO)	-43.10
C_(C)(C)(Cl)(Cl)	-22.00	C_(CO)(Cl)(Cl)(Cl)	-11.80	O_(C)(NO2)	-19.40
C_(C)(C)(CO)	-1.70	C_(CO)(CO)	-7.60	O_(C)(O)	-4.50
C_(C)(C)(F)	-49.00	C_(I)(O)	3.80	O_(C*)	-37.90
C_(C)(C)(F)(F)	-97.00	C_(O)	-10.20	O_(Cd)(Cd)	-33.00
C_(C)(C)(I)	10.50	C_(O)(O)	-16.10	O_(Cd)(CO)	-45.20
C_(C)(C)(NO2)	-13.60	Cd_(C)(C)(Cd)	10.34	O_(CO)	-58.10
C_(C)(C)(O)	-7.20	Cd_(C)(Cd)	8.59	O_(CO)(CO)	-46.50
C_(C)(C)(O)(O)	-18.60	Cd_(C)(Cd)(Cd)	8.88	O_(CO)(O)	-19.00
C_(C)(C)(O*)	7.80	Cd_(C)(Cd)(CO)	7.50	O_(NO2)(O)	4.00
C_(C)(C*)	-4.95	Cd_(C)(Cd)(O)	10.30	O_(O)	-16.30
C_(C)(C*)(C)	-1.90	Cd_(Cd)	6.26	O_(O)(O)	14.70
<u>Assigned to Zero</u>					
*CO_(C)	0.00	Cl_(CO)	0.00	NO2_(C)	0.00
Br_(C)	0.00	F_(C)	0.00	NO2_(O)	0.00
Br_(C*)	0.00	F_(CO)	0.00	ONO2_(C)	0.00
Br_(CO)	0.00	I_(C)	0.00		
Cl_(C)	0.00	I_(CO)	0.00		

Table 38. Thermochemical group assignments used for estimating heats of reaction for rate constant estimation purposes that were derived for this work. Estimation methods and notation based on Benson (1976).

Group	kcal/mole	Documentation [a]
*CO_(O)	-4.20	C-H bond energy in formates is estimated to be 95 kcal/mole or higher based on correlation between BDE and CO-H + OH rate constants.
*CO_(ONO2)	-19.40	Calculated from O_(C)(NO2) + *CO_(O), *CO_(O) assignment: Assigned
C*(Br)(C)	41.78	Estimated using correlation between kOH and BDE for alkanes and methanol, and kOH estimated using group additivity.
C*(C)(C)(CO)	42.25	Estimated using: force-hr $\text{ch3-c[.](ch3)-cho} + \text{ch3-ch2-cho} = \text{ch3-ch(ch3)-cho} + \text{ch3-ch[.]-cho}$
C*(C)(C)(O)	31.50	Estimated using: force-hr $\text{ch3-c[.](ch3)oh} + \text{ch3-ch(ch3)ch3} + \text{ch3-ch2-oh} + \text{ch3-ch[.]-ch3} = \text{ch3-ch(ch3)oh} + \text{ch3-c[.](ch3)ch3} + \text{ch3-ch[.]-oh} + \text{ch3-ch2-ch3}$
C*(C)(C)(ONO2)	12.10	Estimated using: force-hr $\text{CH3-C[.](ONO2)-CH3} = \text{CH3-C[.](O-NO2)-CH3}$
C*(C)(CO)	38.58	Estimated using: force-hr $\text{ch3-co-ch2.} + \text{ch3-ch2-co-ch3} + \text{ch3-ch2-ch3} + \text{ch3-ch2-ch[.]-ch3} = \text{ch3-co-ch3} + \text{ch3-ch[.]-co-ch3} + \text{ch3-ch2-ch2.} + \text{ch3-ch2-ch2-ch3}$
C*(C)(CO)(O)	32.46	Assumed to be the same as normal secondary alcohols, i.e., that carbonyl group does not affect BDE.
C*(C)(O)(O)	24.50	Estimated using: force-hr $\text{HO-CH(CH3)-OH} + \text{HO-CH[.]-CH3} = \text{HO-C[.](CH3)-OH} + \text{HO-CH2-CH3}$
C*(C)(ONO2)	15.70	Calculated from O_(C)(NO2) + C*(C)(O)
C*(CO)(O)	34.95	Assumed to be the same as normal primary alcohols, i.e., that carbonyl group does not affect BDE.
C*(CO)(ONO2)	15.55	Estimated using: FORCE-HR $\text{HCO-CH[.]-ONO2} = \text{HCO-CH[.]-O-NO2}$
C*(O)	35.75	WPC: Was 33.7. Adjusted to agree with Hf (.CH2OH) given by IUPAC (1996)
C*(O)(O)	29.93	Estimated using: force-hr $\text{HO-CH2-OH} + \text{HO-CH2.} = \text{HO-CH[.]-OH} + \text{HO-CH3}$
C*(ONO2)	16.35	Calculated from O_(C)(NO2) + C*(O), C*(O) assignment: WPC: Was 33.7. Adjusted to agree with Hf (.CH2OH) given by IUPAC (1996)
C_(*CO)(C)(C)(C)	5.70	$\text{CH3-C(CH3)(CH3)-CHO}$ assumed to have the same CO..H BDE as $\text{CH3-CH(CH3)-CHO}$ .
C_(*CO)(C)(ONO2)	-20.53	$\text{CH3-CH(ONO2)-CHO}$ is assumed to have the same (CO)..H BDE as $\text{CH3-CH2-CHO}$ .
C_(*CO)(CO)	-2.41	$\text{HCO-CH2-CHO}$ is assumed to have the same (CO)..H BDE as $\text{CH3-CH2-CHO}$ .
C_(*CO)(O)	-1.76	$\text{CH3-O-CH2-CHO}$ is assumed to have the same (CO)..H BDE as $\text{CH3-CH2-CHO}$ .
C_(*CO)(ONO2)	-21.17	ref $\text{HCO-CH2-ONO2}$ assumed to have same (CO)..H BDE as $\text{CH3-CH2-CHO}$ .
C_(Br)(C)(CO)	4.00	Reaction $[\text{ch3-ch(cho)-br} + \text{ch3.} = \text{ch3-ch(cho)-ch3} + \text{br.}]$ is assumed to have same HR as analogous reactions for $\text{CH3-CH(Cl)-Br}$ .
C_(Br)(C)(O)	-2.50	Reaction $[\text{ch3-ch(oh)-br} + \text{ch3.} = \text{ch3-ch(oh)-ch3} + \text{br.}]$ is assumed to have same HR as analogous reactions for $\text{CH3-CH(Cl)-Br}$ .
C_(Br)(C)(O*)	12.50	Reaction $[\text{ch3-ch[o.]-br} + \text{ch3.} = \text{ch3-ch[o.]-ch3} + \text{br.}]$ is assumed to have same HR as analogous reactions for $\text{CH3-CH(Cl)-Br}$ .
C_(Br)(C*)	-6.67	Reaction $[\text{.ch2-ch2-br} + \text{ch3.} = \text{.ch2-ch2-ch3} + \text{br.}]$ is assumed to have same HR as analogous reactions for alkyl groups.
C_(Br)(CO)	-6.27	Reaction $[\text{ch3-co-ch2-br} + \text{ch3.} = \text{ch3-co-ch2-ch3} + \text{br.}]$ is assumed to have same HR as analogous reactions for alkyl groups.
C_(Br)(O)	-3.70	Estimated using: force-hr $\text{br-ch2o.} + \text{ch3-oh} = \text{br-ch2-oh} + \text{ch3o.}$
C_(Br)(O*)	10.79	Reaction $[\text{.och2-br} + \text{ch3.} = \text{.och2-ch3} + \text{br.}]$ is assumed to have same HR as analogous reactions for $\text{CH3-CH(Cl)-Br}$ .

Table 38 (continued)

Group	kcal/mole	Documentation [a]
C_(Br)(OO*)	9.30	Estimated using: force-hr br-ch2oo. + ch3-o-oh = br-ch2-o-oh + ch3oo.
C_(C)(C)(C)(C*)	-1.20	Estimated using: force-hr ch3-c(ch3)(ch3)-ch3 = ch3-c(ch3)(ch3)ch2. + h. is 99.7
C_(C)(C)(C)(ONO2)	-26.00	Calculated from O_(C)(NO2) + C_(C)(C)(C)(O)
C_(C)(C)(C)(OO*)	5.50	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(C)(C)(C*)	-3.60	Estimated using: force-hr ch3-ch(ch3)ch3 = ch3-ch(ch3)ch2. + h. is 99.7
C_(C)(C)(C*)(O)	-8.90	Estimated using: force-hr ch3-c(ch3)(oh)-ch2. + ch3-ch(oh)-ch3 = ch3-c(ch3)(oh)-ch3 + ch3-ch(oh)-ch2.
C_(C)(C)(C*)(ONO2)	-28.30	Estimated using: force-hr .CH2-C(CH3)(CH3)-ONO2 = .CH2-C(CH3)(CH3)-O-NO2
C_(C)(C)(CO)(CO)	-1.47	Estimated using: force-hr hco-ch(ch3)-cho + ch3-c(ch3)(ch3)-cho = hco-c(ch3)(ch3)-cho + ch3-ch(ch3)-cho
C_(C)(C)(CO)(O)	-5.70	Estimated using: force-hr ch3-c(oh)(ch3)-cho + ch3-c(ch3)(ch3)ch3 = ch3-c(ch3)(ch3)cho + ch3-c(oh)(ch3)-ch3
C_(C)(C)(CO)(O*)	9.50	Estimated using: force-hr ch3-c(oh)(ch3)cho + ch3-c[o.](ch3)ch3 = ch3-c[o.](ch3)cho + ch3-c(oh)(ch3)ch3
C_(C)(C)(CO)(ONO2)	-25.10	Estimated using: force-hr CH3-C(CH3)(ONO2)-CO-CH3 = CH3-C(CH3)(O-NO2)-CO-CH3
C_(C)(C)(O)(O*)	-3.40	Assumed to have same O..H BDE as t-butanol
C_(C)(C)(O)(ONO2)	-38.00	Calculated from O_(C)(NO2) + C_(C)(C)(O)(O)
C_(C)(C)(O)(OO*)	-6.50	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(C)(C)(O*)(ONO2)	-23.80	Calculated from O_(C)(NO2) + C_(C)(C)(O)(O*), C_(C)(C)(O)(O*) assignment: WPC: Assumed to have same BDE as used for C_CCHO*
C_(C)(C)(ONO2)	-26.60	Calculated from O_(C)(NO2) + C_(C)(C)(O)
C_(C)(C)(OO*)	4.90	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(C)(C*)(CO)	-3.40	Estimated using: force-hr ch3-co-ch(ch3)-ch2. + ch3-ch(ch3)-ch3 = ch3-co-ch(ch3)-ch3 + ch3-ch(ch3)-ch2.
C_(C)(C*)(CO)(O)	-8.00	Estimated using: force-hr ch3-o-c(ch3)(cho)-ch2. + ch3-o-c(ch3)(ch3)-ch3 = ch3-o-c(ch3)(cho)-ch3 + ch3-o-c(ch3)(ch3)-ch2.
C_(C)(C*)(CO)(ONO2)	-27.40	HCO-C(CH3)(ONO2)-CH3 is assumed to have same CH2..H BDE as HCO-C(CH3)(OH)-CH3.
C_(C)(C*)(O)	-9.50	WPC: Assumed to have BDE of 100 (between ethane and propane)
C_(C)(C*)(ONO2)	-28.90	Calculated from O_(C)(NO2) + C_(C)(C*)(O), C_(C)(C*)(O) assignment: WPC: Assumed to have BDE of 100 (between ethane and propane)
C_(C)(Cd)(ONO2)	-25.90	Calculated from O_(C)(NO2) + C_(C)(Cd)(O)
C_(C)(Cl)(O*)	-6.60	Reaction [ch3-ch[o.]-cl + ch3. = ch3-ch[o.]-ch3 + cl.] Is assumed to have same HR as analogous reactions of compounds with the C_ClHO group.
C_(C)(Cl)(ONO2)	-41.00	Calculated from O_(C)(NO2) + C_(C)(Cl)(O)
C_(C)(CO)(CO)	-4.57	Estimated using: force-hr ch3-co-ch2-co-ch3 + ch3-ch2-ch(ch3)-ch2-ch3 = ch3-co-ch(ch3)-co-ch3 + ch3-ch2-ch2-ch2-ch3
C_(C)(CO)(CO)(O)	-8.57	Estimated using: force-hr hco-c(ch3)(oh)-cho + hco-c(ch3)(ch3)-ch3 = hco-c(ch3)(ch3)-cho + hco-c(ch3)(oh)-ch3
C_(C)(CO)(O)	-6.32	WPC: Estimated assuming Hr (ch3-ch2-oh + ch3-cho -> ch3-ch3 + hoch2-cho) = Hr (ch3-ch(oh)-ch3 + ch3-ch2-cho -> ch3-ch(oh)-cho + ch3-ch2-ch3). Depends on C_(CO)OHH
C_(C)(CO)(O)(O)	-17.70	Estimated using: force-hr ch3-o-c(cho)(ch3)-o-ch3 + ch3-o-c(ch3)(ch3)-ch3 = ch3-o-c(ch3)(ch3)-o-ch3 + ch3-o-c(cho)(ch3)-ch3



Table 38 (continued)

Group	kcal/mole	Documentation [a]
C_(C)(CO)(O)(O*)	-2.50	Assumed to have the same O..H BDE as other tertiary alcohols.
C_(C)(CO)(O*)	7.87	WPC: H-O BDE of 104.2 assumed
C_(C)(CO)(ONO2)	-25.72	Estimated using: force-hr CH3-CH(ONO2)-CO-CH3 = CH3-CH(O-NO2)-CO-CH3
C_(C)(NO2)(NO2)	-9.90	DIPPR value -16.5, No Benson H-value, this from literature [6]
C_(C)(O)(O)(ONO2)	-49.00	Calculated from O_(C)(NO2) + C_(C)(O)(O)(O)
C_(C)(O)(O*)	-2.10	WPC: Assumed to have same BDE as CH3-CH2-CH2-O
C_(C)(O)(ONO2)	-35.70	Calculated from O_(C)(NO2) + C_(C)(O)(O)
C_(C)(O)(OO*)	-4.20	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH3OO. and C2H5OO.
C_(C)(O*)(ONO2)	-21.50	Calculated from O_(C)(NO2) + C_(C)(O)(O*), C_(C)(O)(O*) assignment: WPC: Assumed to have same BDE as CH3-CH2-CH2-O
C_(C)(ONO2)	-27.50	Calculated from O_(C)(NO2) + C_(C)(O)
C_(C)(OO*)	3.34	Based on IUPAC Hf for CH3-CH2OO.
C_(C*)(Cl)	-18.01	Reaction [.ch2-ch2-cl + ch3. = .ch2-ch2-ch3 + cl.] is assumed to have same HR as analogous reactions of chloroalkanes.
C_(C*)(CO)	-6.90	WPC: H-CH2-CH2-CHO assumed to have same BDE as propane.
C_(C*)(CO)(O)	-8.02	Estimated using: force-hr HCO-CH(CH2.)OH + ch3-ch(ch3)ch3 = hco-ch(ch3)oh + ch3-ch(ch2.)ch3
C_(C*)(CO)(ONO2)	-27.42	HCO-CH(ONO2)-CH3 is assumed to have same CH2..H BDE as HCO-CH(OH)-CH3.
C_(C*)(O)	-9.73	WPC: Estimated assuming same BDE as n-propyl.
C_(C*)(O)(O)	-18.60	BDE for CH3-O-CH(OH)-CH2..H is assumed to be the same as for CH3-CH(OH)-CH2...H.
C_(C*)(ONO2)	-29.13	Calculated from O_(C)(NO2) + C_(C*)(O), C_(C*)(O) assignment: WPC: Estimated assuming same BDE as n-propyl.
C_(Cd)(O)	-8.05	Missing from NIST table. Set to give same estimated HF for CH2=CH-CH2-OH as NIST
C_(Cd)(O*)	5.25	CH2=CH-CH2-OH is assumed to have the same O..H BDE as other primary alcohols.
C_(Cd)(OO*)	3.39	Allylic hydroperoxides assumed to have same O..H BDE as alkyl hydroperoxides.
C_(Cl)(Cl)(O*)	-10.10	Reaction [cl-ch[o.]-cl + ch3. = cl-ch[o.]-ch3 + cl.] is assumed to have same HR as analogous reactions for dichloroalkanes.
C_(CO)(CO)(O)	-9.19	Estimated using: force-hr hco-ch(oh)-cho + hco-ch(ch3)-ch3 = hco-ch(ch3)-cho + hco-ch(oh)-ch3
C_(CO)(CO)(O*)	5.81	Assumed to have same O..H BDE as other secondary alcohols.
C_(CO)(CO)(ONO2)	-28.59	Estimated using: force-hr HCO-CH(ONO2)-CHO = HCO-CH(O-NO2)-CHO
C_(CO)(O)	-6.95	WPC: Estimated assuming Heat of reaction of -CO-CH2-CO- + CH2Cl2 = 2 -CO-CH2-Cl is the same as that for -CO-CH2-CO- + -O-CH2-O- = 2 -CO-CH2-O-.
C_(CO)(O)(O)	-15.42	Estimated using: force-hr hco-ch(oh)-o-ch3 + ch3-ch(oh)-ch3 = hco-ch(oh)-ch3 + ch3-ch(oh)-o-ch3
C_(CO)(O)(O*)	-1.22	CH3-O-CH(OH)-CO-CH3 is assumed to have the same O..H BDE as CH3-CH2-CH2-OH.
C_(CO)(O*)	7.24	WPC: Assumed to have same BDE as CH3-CH2-CH2-O. Note that this depends on highly uncertain assignment for C(CO)HHO.
C_(CO)(ONO2)	-26.36	Calculated from O_(C)(NO2) + C_(CO)(O), C_(CO)(O) assignment: WPC: Estimated assuming Heat of reaction of -CO-CH2-CO- + CH2Cl2 = 2 -CO-CH2-Cl is the same as that for -CO-CH2-CO- + -O-CH2-O- = 2 -CO-CH2-O-.
C_(CO)(OO*)	6.05	Estimated using: force-hr ch3-co-ch2-o-oh + ch3oo. = ch3-co-ch2oo. + ch3-o-oh
C_(I)(ONO2)	-15.60	Calculated from O_(C)(NO2) + C_(I)(O)

Table 38 (continued)

Group	kcal/mole	Documentation [a]
C_(O)(O)(O)	-26.92	Based on average of the heats of formation of trimethoxy methane tabulated by NIST at <a href="http://webbook.nist.gov/">http://webbook.nist.gov/</a>
C_(O)(O)(O)(O)	-40.25	Based on average of the heats of formation of tetramethoxy methane tabulated by NIST at <a href="http://webbook.nist.gov/">http://webbook.nist.gov/</a>
C_(O)(O)(O)(O*)	-25.05	Assumed to have same O..H BDE as other tertiary alcohols.
C_(O)(O*)	-1.90	WPC: Assumed to have same BDE as CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O
C_(O)(ONO <sub>2</sub> )	-35.50	Calculated from O_(C)(NO <sub>2</sub> ) + C_(O)(O)
C_(O)(OO*)	-4.00	BDE for ROO..H assumed to be 85.0 based on IUPAC Hf's for CH <sub>3</sub> OO. and C <sub>2</sub> H <sub>5</sub> OO.
C_(O*)(ONO <sub>2</sub> )	-21.30	Calculated from O_(C)(NO <sub>2</sub> ) + C_(O)(O*), C_(O)(O*) assignment: WPC: Assumed to have same BDE as CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O
C_(ONO <sub>2</sub> )	-29.60	Calculated from O_(C)(NO <sub>2</sub> ) + C_(O)
C_(OO*)	2.49	Estimated using IUPAC (1996) Hf's for CH <sub>3</sub> OOH and CH <sub>3</sub> OO.
CO_(Br)	-25.73	Reaction [hco-br + ch <sub>3</sub> . = hco-ch <sub>3</sub> + br.] is assumed to have same HR as analogous reactions for CH <sub>3</sub> -CH(Cl)-Br.
CO_(Br)(C)	-27.81	Reaction [ch <sub>3</sub> -co-br + ch <sub>3</sub> . = ch <sub>3</sub> -co-ch <sub>3</sub> + br.] is assumed to have same HR as analogous reactions for CH <sub>3</sub> -CH(Cl)-Br.
CO_(C)(Cd)	-34.06	Derived to fit HF in NIST database for CH <sub>2</sub> =CH-CO-CH <sub>3</sub> .
CO_(C)(O*)	-39.36	WPC: Derived from IUPAC Hf for ch <sub>3</sub> cooh, and CRC O..H BDE.
CO_(C)(OO*)	-30.91	Derived using IUPAC Hf for ch <sub>3</sub> -c(o)oo.
CO_(C*)	-29.10	WPC: Assumed to have same BDE as used for ch <sub>3</sub> -co-ch <sub>2</sub> .
CO_(C*)(O)	-34.10	Estimated using correlation between kOH and BDE for alkanes and methanol, and kOH estimated using group additivity.
CO_(Cl)	-45.84	Reaction [hco-cl + ch <sub>3</sub> . = hco-ch <sub>3</sub> + cl.] Is assumed to have same HR as analogous reaction of R-CO-Cl
CO_(Cl)(ONO <sub>2</sub> )	-68.60	Calculated from O_(C)(NO <sub>2</sub> ) + CO_(Cl)(O)
CO_(CO)(CO)	-26.89	Hr for elimination of CO from CH <sub>3</sub> -CO-CO-CO-CH <sub>3</sub> is assumed to be the same as for elimination of CO from biacetyl.
CO_(O)(O*)	-34.10	Estimated using: force-hr ch <sub>3</sub> -co-oh + ch <sub>3</sub> -o-co <sub>2</sub> . = ch <sub>3</sub> -co <sub>2</sub> . + ch <sub>3</sub> -o-co-oh
CO_(O)(OO*)	-25.51	BDE for ch <sub>3</sub> -o-co-oo..h Assumed to be same as for ch <sub>3</sub> -co-oo..h.
CO_(O*)	-36.84	Estimated using: force-hr ch <sub>3</sub> -co-oh + hco <sub>2</sub> . = ch <sub>3</sub> -co <sub>2</sub> . + hco-oh
O_(*CO)	-42.64	HCO-OH is assumed to have same (CO)..H BDE as CH <sub>3</sub> -O-CHO.
O_(*CO)(C)	-27.30	WPC: BDE for H-CO-O-R estimated to be relatively high (~100) based on low OH radical rate constant. Highly uncertain.
O_(C*)(CO)	-40.65	WPC: H-CH <sub>2</sub> -O-CO- assumed to have same BDE as ethane.
O_(C*)(NO <sub>2</sub> )	-12.45	Estimated using correlation between kOH and BDE for alkanes and methanol, and kOH estimated using group additivity.
O_(C*)(O)	-4.50	Estimated using: force-hr *ch(ch <sub>3</sub> )-o-c[.](ch <sub>3</sub> )-o-o-o-* + ho-ch <sub>2</sub> -ch <sub>3</sub> = *ch(ch <sub>3</sub> )-o-ch(ch <sub>3</sub> )-o-o-o-* + ho-ch[.]-ch <sub>3</sub>
O_(Cd)	-44.86	Derived to fit HF in NIST database for CH <sub>2</sub> =CH-OH (-30).
O_(O)(O*)	17.50	Estimated using: force-hr ch <sub>3</sub> -o-o-oh + ch <sub>3</sub> oo. = ch <sub>3</sub> -o-o-o. + ch <sub>3</sub> -o-oh
O_(O*)(ONO <sub>2</sub> )	14.00	Calculated from O_(C)(NO <sub>2</sub> ) + O_(O)(O*)
ONO <sub>2</sub> _(C*)	6.95	Estimated using: force-hr .ch <sub>2</sub> -ono <sub>2</sub> = .ch <sub>2</sub> -o-no <sub>2</sub>

[a] The documentation text in this version is preliminary. These will be cleaned up for the final draft, and footnotes will be added to explain the notation used.

Note that there were insufficient resources in this project to comprehensively review the available and most up-to-date thermochemical group data, so some of the assignments shown on Table 38 may not necessarily represent the state of the art, and they probably can be improved significantly in some cases. However, given the other uncertainties of the estimation methods discussed above, it is suspected that this probably does not represent the largest source of uncertainty involved, at least in most cases.

The more significant problem with the thermochemical assignment database in the current mechanism generation system is a lack of assignments for certain groups, which limits the overall scope of the mechanism generation system. In particular, the limited number of assignments for halogenated groups (particularly those containing radicals) means that mechanisms cannot be generated for most halogenated compounds. Also, the lack of assignments for unsaturated radicals means the system cannot automatically generate mechanisms for abstraction reactions from alkenes [which are believed to be non-negligible for longer chain alkenes (Atkinson, 1997a)] or reactions of OH or NO<sub>3</sub> radicals with dialkenes. Lack of thermochemical group estimates also prevents mechanisms from being generated for certain highly substituted groups as well. Because of this, improving the thermochemical database needs to be a priority when this system is updated.

## 11. Reactions of Crigee Biradicals

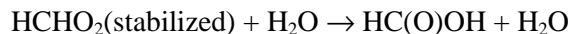
Crigee biradicals, i.e., species of the type  $>C[·]OO·$ , are assumed to be formed in the reactions of O<sub>3</sub> with alkenes or alkynes, and by the reactions of carbenes (that are assumed to be formed in the photolyses of some unsaturated compounds) with O<sub>2</sub>. These radicals are believed to be formed with initial vibrational excitation, and can undergo various unimolecular decompositions or be collisionally stabilized. The ranges of excitation energies of the biradicals formed from the reactions of carbenes with O<sub>2</sub> or O<sub>3</sub> with alkynes are almost certainly different from those formed in the reactions of O<sub>3</sub> with alkenes, so in general one might expect the branching ratios for the decomposition and stabilization routes to differ depending on the source of the biradicals. However, because of lack of information concerning the former reactions we assume that they react with the same mechanism as determined from O<sub>3</sub> + alkene systems.

### a. HCHO<sub>2</sub> Biradicals

Atkinson (1997a) reviewed available information concerning reactions of O<sub>3</sub> with alkenes, and recommended the following mechanisms for the reactions of excited HCHO<sub>2</sub> biradicals:

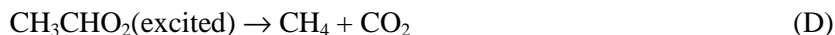
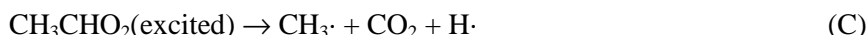
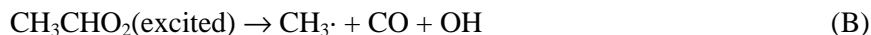
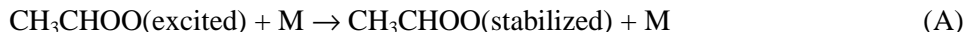


These branching ratios are used in the current mechanism. As indicated in Section II.A.2.b, the stabilized biradicals are assumed to react primarily with H<sub>2</sub>O, forming the corresponding acid, i.e.,



## b. RCHO<sub>2</sub> Biradicals

The reactions of substituted Crigiee biradicals are more uncertain. In the case of excited CH<sub>3</sub>CHO<sub>2</sub>·, the following routes, discussed by Atkinson (1997a), appear to be the most reasonable to consider<sup>13</sup>:



Based on examination of the available literature, Atkinson (1997a) recommends assuming branching ratios of 15%, 54%, 17%, and 14% for pathways A-D, respectively. In the case of other substituted biradicals, this scheme can be generalized to



Note that Pathway B can account for much of the OH radical formation observed in the reactions of O<sub>3</sub> with 1-alkenes. The measured yields of OH radicals from the reactions of O<sub>3</sub> with 1-butene through 1-octene, as summarized by Atkinson (1997a) (see also Table 18, above), do not appear to be greatly different from that for the reaction of O<sub>3</sub> with propene, suggesting that the branching ratios may not change as the size of the biradical increases.

However, as discussed in Section ??, assuming the relatively high branching ratios recommended by Atkinson (1997a) for Pathways B and C results in positive biases in model simulations of the large data base of propene - NO<sub>x</sub> environmental chamber experiments, and in significant overpredictions of O<sub>3</sub> formation rates in 1-butene - NO<sub>x</sub> and (especially) 1-hexene - NO<sub>x</sub> environmental chamber experiments. Although there are other uncertainties in the mechanisms that could be causing these discrepancies, reasonably consistent fits to the data cannot be obtained unless it is assumed that (1) somewhat lower radical yields (i.e., lower yields of Pathways B and C) are assumed for the excited CH<sub>3</sub>CHOO reactions than recommended by Atkinson (1997a), and (2) the radical yields (i.e., the yields of Pathways B' and C') decrease as the size of the molecule increases. Note that both assumptions are inconsistent with the observed OH yields in the reactions of O<sub>3</sub> with 1-alkenes (Atkinson, 1997a – see also Table 18, above), so there is an apparent inconsistency between the laboratory measurements of the OH yields in the O<sub>3</sub> + alkene reactions and the results of modeling the 1-alkene - NO<sub>x</sub> chamber experiments used to evaluate the mechanism.

The reason for this apparent inconsistency is unknown, and it might be due in part to the fact that NO<sub>x</sub> is present in the environmental chamber experiments but not in the laboratory systems used to measure the OH yields. However, the possibility that the problems with modeling the 1-alkene

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<sup>13</sup> Two other routes, involving formation of CH<sub>3</sub>O· + HCO and CH<sub>3</sub>OH + CO, are also given by Atkinson (1997a), but are not considered here because they do not involve chemically reasonable transition states for vibrationally excited molecules.

chamber experiments using the Atkinson (1997a)-recommended branching ratios are due to other problems with the mechanism certainly cannot be ruled out. Nevertheless, as discussed in Section ??, satisfactory fits to the available data cannot be obtained even after adjusting or making reasonable modifications in the other uncertain aspects of the alkene photooxidation mechanisms. Because the objective of this project is to develop a mechanism that correctly predicts O<sub>3</sub> reactivities and other impacts of VOCs in simulated smog systems, it is necessary to use branching ratios that give predictions that are consistent with the large environmental chamber data.

The adjusted branching ratios for the reactions of excited RCHO<sub>2</sub> biradicals that are used in the current version of the mechanism are summarized on Table 39. As shown there, to fit the chamber data the biradicals are assumed to be increasingly likely to be stabilized as the size of the “R” substituent on the radical is increased. For this purpose, the “size” of the substituent is defined as the number of groups used by the mechanism generation system to define the substituent, as indicated in Table 5, above. Note that for biradicals formed from unsubstituted alkenes the number of groups is the same as the number of carbons. Footnotes to the table indicate the rationalizations for the particular sets of branching ratios used.

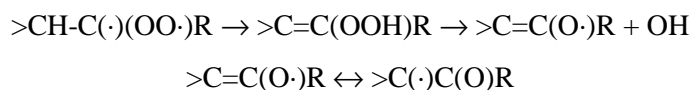
Table 39. Adjusted branching ratios used for the reactions of excited RCHO<sub>2</sub> biradicals.

Pathway	Number of Groups in R.	Branching Ratio				
		1	2	3	4	5+
Stabilization -> RC(O)OH	(A)	34%	89%	92%	95%	100%
R. + CO + OH	(B)	52%	11%	8%	5%	0%
R. + CO <sub>2</sub> + H	(C)	0%	0%	0%	0%	0%
RH + CO <sub>2</sub>	(D)	14%	0%	0%	0%	0%
Notes		1	2	3	4	5

- 1 OH yield and methane formation (Pathways B and D) approximately as recommended by Atkinson (1997a). Radical formation from Pathway C is assumed to be negligible to improve fits of model simulation to propene - NO<sub>x</sub> chamber experiments, and fraction of stabilization (Pathway A) is increased accordingly.
- 2 Radical formation from Pathway (C) is assumed to be negligible and OH formation from Pathway (B) is reduced to improve fits of model simulations to 1-butene - NO<sub>x</sub> chamber experiments. Rest of reaction is assumed to be stabilization.
- 3 Branching ratios intermediate between those derived for the 1-butene and 1-hexene systems.
- 4 Model simulations are most consistent with results of 1-hexene - NO<sub>x</sub> chamber experiments if radical formation from the reactions of this biradical is assumed to involve no more than ~5% radical formation routes. The rest of the reaction is assumed to involve stabilization.
- 5 100% stabilization is assumed by extrapolation from the mechanisms assumed for the smaller biradicals.

### c. R<sub>2</sub>COO Biradicals

Available information on OH yields from reactions of O<sub>3</sub> with alkenes such as isobutene, 2-methyl-2-butene, 2,3-dimethyl-2-butene and other compounds (Atkinson, 1997a – see also Table 18, above) are most easily rationalized if it is assumed that most excited R<sub>2</sub>COO react forming OH radicals in near-unit yields. In contrast with the case with 1-alkenes, model simulations assuming high radical yields in the reactions of O<sub>3</sub> with such alkenes are also reasonably consistent with the available chamber data, at least in the case of isobutene and several of the terpenes that are expected to form this type of biradical (see Section ??). If one of the R groups has an α hydrogen, the reaction is assumed to proceed via rearrangement to an unsaturated hydroperoxide, which subsequently decomposes (Atkinson, 1997a):



Although other reactions probably occur to some extent, this is assumed to be the dominant reaction pathway for R<sub>2</sub>COO biradicals which have the necessary α hydrogen. It may be that this reaction also occurs with the stabilized biradical, which may explain why there is no indication of decreased OH yield as the size of the molecule increases.

If the two substituents on the biradical are different and both have abstractable  $\alpha$  hydrogens, then two possible OH-forming reactions can occur. In these cases, we estimate that the branching ratio is roughly proportional to the ratio of OH radical abstraction from the abstracted  $\alpha$  hydrogens involved. This is uncertain because there is no experimental basis for this estimate.

The above mechanism cannot occur for those disubstituted Crigee biradicals that do not have substituents with  $\alpha$  hydrogens. It is also considered to be unlikely if the only substituent(s) with  $\alpha$  hydrogens are -CHO groups, since it is expected that formation of a ketene hydroperoxide intermediate would involve a strained transition state. In those cases (which probably do not occur in many cases for the VOCs currently considered in the mechanism), we arbitrarily assume that 90% is stabilized and 10% decomposes to  $\text{CO}_2 + 2 \text{R}\cdot$ .

#### **d. Assigned Reactions of $\alpha$ -Carbonyl or Unsaturated Crigee Biradicals**

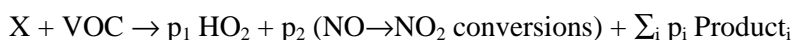
Carter and Atkinson (1996) gave estimated mechanisms for several  $\alpha$ -carbonyl or unsaturated Crigee biradicals that are different from the general mechanisms discussed above. In most cases, these are adopted in this work. These are summarized on Table 40. Note that the reactions shown for  $\text{HC(O)CHOO}$ ,  $\text{CH}_2=\text{CHCHOO}$ , and  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHOO}$  are assigned mechanisms applicable for those biradicals only, while that shown for  $\text{RC(O)CHOO}$  is a general mechanism that is derived based on the mechanism assumed by Carter and Atkinson (1996) for  $\text{CH}_3\text{C(O)CHOO}$ , but is assumed to be applicable for all radicals of this type, regardless of the nature of the “R” group.

Table 40. Assigned mechanisms for the reactions of excited  $\alpha$ -carbonyl or unsaturated Crigiee biradicals.

Reactant and Products	Factor	Documentation
<u>R-CO-CHOO[excited]</u>		
R-COO[excited]-CHO	100.0%	O-shifts of alpha-carbonyl biradicals, via a primary ozonide transition state, are assumed to be rapid if they form a more substituted biradical (Carter and Atkinson, 1996)
<u>CH<sub>2</sub>=C(CH<sub>3</sub>)-CHOO[excited]</u>		
CO <sub>2</sub> + CH <sub>2</sub> =CH-CH <sub>3</sub>	25.0%	As assumed by Carter and Atkinson (1996).
CH <sub>2</sub> =C(CHOO[stab])-CH <sub>3</sub>	75.0%	See above.
<u>CH<sub>2</sub>=CH-CHOO[excited]</u>		
CO <sub>2</sub> + CH <sub>2</sub> =CH <sub>2</sub>	25.0%	Assumed to be analogous to mechanism assumed for methyl-substituted radical formed from O <sub>3</sub> + isoprene (Carter and Atkinson, 1996).
CH <sub>2</sub> =CH-CHOO[stab]	75.0%	See above.
<u>HCO-CHOO[excited]</u>		
CO + HCO. + OH	50.0%	Assumed that decomposition is much more facile than in the CH <sub>3</sub> -CHOO[excited] case because of the weaker H..CO and C..CO bonds. The two most likely decomposition routes are arbitrarily assumed to have equal probability.
HCO <sub>2</sub> . + HCO.	50.0%	See above.

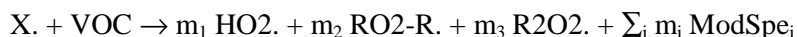
## 12. Lumping Assignments

Once the reactions of a given VOC with OH, NO<sub>3</sub>, O<sub>3</sub>, etc. have been fully generated, the system summarizes the overall yields of all products (including the NO→NO<sub>2</sub> conversion operator), so that each initial reaction of the VOC in the presence of NO<sub>x</sub> can be represented by one overall process



Here X refers to the species reacting with the VOC (OH, hv, etc.), product<sub>i</sub> represents each of the products that are formed, and p<sub>i</sub> represents its overall yield. Since many hundreds and even thousands of products might be formed in the reactions of larger molecules, it is clearly not possible that they all be represented explicitly in the model simulations. As discussed in Section II.A.3, above, the current mechanism represents most oxidation products using a limited number of model species based on various “lumped molecule” assignments.

These assignments, which provide the interface between the mechanism generation system discussed above and the base mechanism discussed in Section II.A, are summarized on Table 41. For each product that is formed in the overall reaction, the system checks the “lumping rules” associated with each model species in the order they are given on this table, and assigns the product to the first model species on the list whose associated rules describe the products being considered. Note that the last model species on the list is “INERT”, which means that if the product satisfies none of the other criteria, it is treated as unreactive in the model. The total yield of each of the model species formed in the overall reaction are then summed up, and the overall reaction is then recast into the form





where HO<sub>2</sub>., RO<sub>2</sub>-R., R<sub>2</sub>O<sub>2</sub>., or ModSpe<sub>i</sub> are model species in the base mechanism (see Table 45 in Appendix A), and m<sub>1</sub>, ..., m<sub>i</sub> are their corresponding yields. Reactions expressed in this way can be inserted directly into the mechanism, or the values of the overall rate constant and product yield parameters (the set of m<sub>i</sub>'s) can serve as a basis for deriving parameters for lumped parameter species used to represent the compound in complex mixtures (see Section ??).

Table 41. Summary of lumping assignments used to determine how individual explicit product species are represented in the base mechanism.

Model Species	Structure or Lumping Criteria
<u>Radical Operators (see text)</u>	
RO2-N.	Any organic nitrate that is formed in a RO2 + NO reaction
Total HO2	HO2.
Total NO->NO2	NO->NO2 conversion operator
<u>Explicit Radicals</u>	
CCO-O2.	CH3-CO[OO.]
C-O2.	CH3OO.
HO.	OH
Cl.	Cl.
TBU-O.	CH3-C[O.](CH3)-CH3
<u>Lumped Radicals</u>	
MA-RCO3.	Any compound containing a C=C double-bonded group next to a CO[OO.] group.
RCO-O2.	Any other compound containing a CO[OO.] group.
<u>Explicit Products</u>	
HNO3	HNO3
NO2	NO2
CO	CO
CO2	CO2
HCHO	HCHO
ACET	CH3-CO-CH3
GLY	HCO-CHO
<u>Lumped Products</u>	
CCHO	CH3-CHO or HO-CH2-CHO
HCOOH	CH2OO[stab] or HCO-OH
CCO-OH	CH3-CHOO[stab] or CH3-CO-OH
MGLY	Any compound containing a -CO- next to a -CHO group.
BACL	Any compound containing a -CO- next to another -CO- group.
METHACRO	CH2=C(CHO)-CH3 or CH2=CH-CHO
MVK	Any compound containing CH2=CH-CO- groups except as indicated above.
ISOPROD	Any compound containing a C=C double-bonded group next to a -CHO or -CO- group except as indicated above, or 3-methyl furan.
RCHO	Any compound containing a -CH2-, >CH- or >C< group next to a -CHO group.
RCO-OH	Any compound containing a -CHOO[stab] group or a -CO- group next to a -OH group.
RNO3	Any compound containing a -ONO2 group that reacts with OH faster than $5 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , that is not formed in a peroxy + NO reaction.
XN	Any other compound containing a -ONO2 group except as indicated above.
PROD2	Anything that reacts with OH faster than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , except as indicated above.
MEK	Anything that reacts with OH faster than $5 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , except as indicated above.
INERT	Anything not satisfying any of the above criteria

Although most of Table 41 is reasonably self-explanatory, some explanation is needed concerning how overall yields of HO<sub>2</sub>., RO<sub>2</sub>-R., R<sub>2</sub>O<sub>2</sub>., and RO<sub>2</sub>-N. are determined. In the case of RO<sub>2</sub>-N., just determining if the product contains a nitrate (-ONO<sub>2</sub>) group is not always appropriate, since the starting reactant itself may contain nitrate groups, and nitrate-containing species are formed when NO<sub>3</sub> reacts with double bonds. Because of this, the system stores a flag with the product log whenever a RO<sub>2</sub>+NO reaction forming a nitrate is generated, which can be used to determine if it is appropriate to represent the product by RO<sub>2</sub>-N. In the case of HO<sub>2</sub>., RO<sub>2</sub>-R., and RO<sub>2</sub>-N., the total yields are computed from the total HO<sub>2</sub> and total NO→NO<sub>2</sub> counts as follows:

Condition:	$[\text{Total HO}_2] \geq [\text{Total NO} \rightarrow \text{NO}_2]$	$[\text{Total NO} \rightarrow \text{NO}_2] > [\text{Total HO}_2]$
HO <sub>2</sub> . Yield =	$[\text{Total HO}_2] - [\text{Total NO} \rightarrow \text{NO}_2]$	0
RO <sub>2</sub> -R. yield =	$[\text{Total NO} \rightarrow \text{NO}_2]$	$[\text{Total HO}_2]$
R <sub>2</sub> O <sub>2</sub> . Yield =	0	$[\text{Total NO} \rightarrow \text{NO}_2] - [\text{Total HO}_2]$

Note that this is an approximate treatment, since the system lumps HO<sub>2</sub> that is formed with no NO to NO<sub>2</sub> conversions (e.g., in reactions of alcohols forming α-hydroxy alkyl groups) with extra NO to NO<sub>2</sub> conversions from another reaction pathway. However, the effect of this approximation should be small, and would only be non-negligible under low NO<sub>x</sub> conditions where peroxy + peroxy reactions convert with NO to NO<sub>2</sub> conversion processes.

## C. Parameterized Mechanisms

The mechanism generation system discussed in the previous system cannot be used for VOCs where the nature of the radical intermediates are unknown, or that involve formation of intermediates that cannot be processed by the present system. These include the aromatics (whose intermediates are highly uncertain and almost certainly involve highly unsaturated radicals for which thermochemical estimates cannot be made), terpenes (whose polycyclic structure cannot be represented by the current system), halogenated compounds (for which insufficient thermochemical information is available on the current database implemented with the system), and compounds containing groups, such as amines, for which general estimation methods have not been developed.

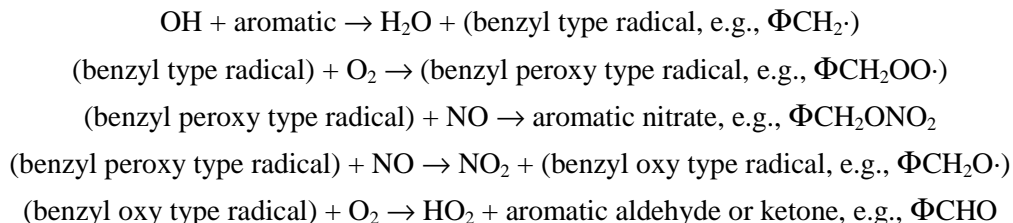
These VOCs must continue to be represented by parameterized or highly simplified mechanisms, as is the case in other mechanisms and previous versions of this mechanism. The representation and mechanisms used in these cases are discussed in this section.

### 1. Representation of Aromatics

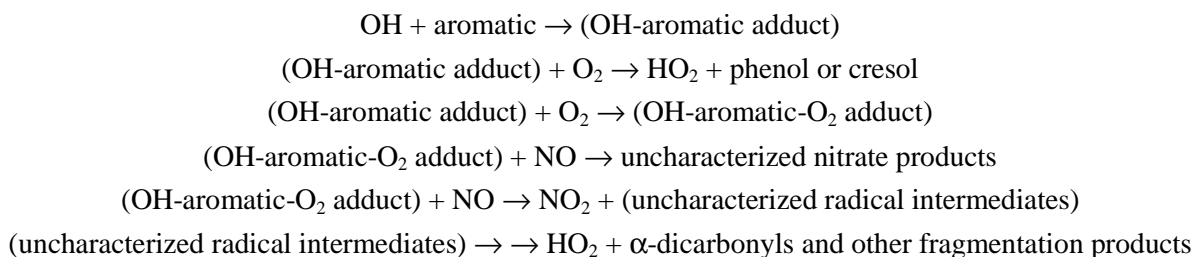
Aromatic hydrocarbons are believed to react in the atmosphere primarily with OH radicals, forming a variety of ring-containing and fragmentation products (Atkinson, 1990, 1999, and references therein). Despite progress in recent years towards improving our understanding of the atmospheric chemistry of aromatic hydrocarbons (e.g., see Atkinson, 1999, and references therein), there is still insufficient understanding of the details of these mechanisms to derive, or even estimate, predictive mechanisms. Therefore, it is still necessary to use parameterized mechanisms, with yields of model species representing reactive uncharacterized products adjusted to fit chamber data, in order to represent the atmospheric reactions of this important class of compounds.

All current photochemical mechanisms are based on assuming that the reactions of OH radicals with aromatics involve two initial processes. The first, which is applicable only for aromatics with

substituents about the ring, involves H-atom abstraction from the side group, ultimately forming primarily aromatic aldehydes and ketones, and possibly small yields of aromatic nitrates as well:

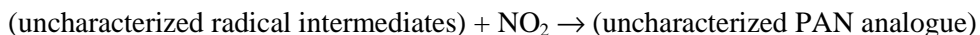


The other reaction route, which is generally the more important (and also the most uncertain), involves addition of OH to the aromatic ring, ultimately forming phenols or cresols to some extent, but primarily forming various ring fragmentation products:



Alternative mechanism formulations, e.g., assuming the OH-aromatic reacts with NO<sub>2</sub> at a rate competing with or exceeding its reaction with O<sub>2</sub>, assuming radical intermediates react with NO<sub>2</sub> to form stable products, or assuming that additional NO to NO<sub>2</sub> conversions are involved in the formation of α-dicarbonyls or other fragmentation products, can also be considered. However, except for the naphthalenes and tetralin (discussed below), experience has shown that parameterizations based on these alternative mechanisms do not fit the available environmental chamber data as well as those based on the general reaction schemes shown above.

The exception to this general scheme is that as discussed below improved fits of model simulations to chamber data for naphthalene, 2,3-dimethyl naphthalene, and tetralin are obtained if it is assumed that at least some of the uncharacterized radical intermediates react in a manner analogous to a PAN precursor (e.g., acyl peroxy) radicals. This involves radicals where the reaction with NO<sub>2</sub> forming a relatively stable termination product, e.g.,

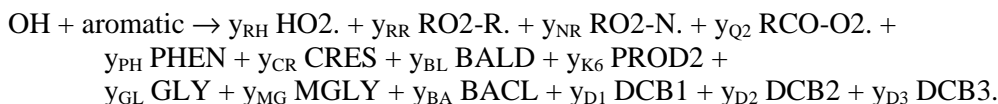


competes with the reaction with NO forming radical propagation products (shown above). The data for these compounds are not fit if it is assumed that there is no significant radical termination process, nor are they well fit if it is assumed that the extent of termination is not strongly affected by reaction conditions. The latter would be the case if the termination were due to organic nitrate formation from the reactions of peroxy radicals with NO, or to the formation of some intermediate, such as phenoxy radicals, that only reacts by a termination process.

Therefore, the parameterization used to represent the reactions of the aromatics in this version is similar to that employed previously (Carter et al, 1997a), except that, as discussed above in Sections II.A.3.a and II.A.3.c, a larger number of model species are used to represent the reactions of the various known and uncharacterized aromatic ring fragmentation projects. In this version, all three of the

$\alpha$ -dicarbonyl products from the methylbenzenes are represented explicitly, and three different model species are used to represent the non-photoreactive (DCB1) and the two types of photoreactive (DCB2 and DCB3) uncharacterized ring fragmentation products. In addition, the mechanisms for the DCB's are are estimated based roughly on those estimated for unsaturated dicarbonyls (see Section II.A.3.c), unlike the previous mechanism where they were based on reactions of  $\alpha$ -dicarbonyls (Carter, 1990). In addition, to at least approximately fit chamber data for the naphthalenes and tetralin, the possibility for the formation of PAN precursor radicals, represented by the RCO-O2· model species, is also included in the parameterization.

In terms of model species used in the current mechanism, the overall reactions of the aromatics are represented as follows:



Here the  $y_{\text{PH}}$ , ...,  $y_{\text{D3}}$  are the stoichiometric parameters that must be specified to define the mechanism. Note that the products shown in the first line represents the formation of various radical products and their effects of NO to NO<sub>2</sub> or organic nitrate formation from reactions of peroxy radicals, those shown in the second line represent the aromatic ring-retaining products (with PROD2 being used to represent aromatic ketones such as methyl phenyl ketone that may be formed from ethylbenzene ), and those in the third line represent the various known or uncharacterized ring fragmentation products.

Note that based on the reaction mechanism formulation discussed above, and considerations of factors such as radical conservation, relationships between some of the parameters can be derived, to reduce the number of parameters that have to be estimated or optimized. Radical conservation requires that

$$y_{\text{RH}} + y_{\text{RR}} + y_{\text{RN}} + y_{\text{Q2}} = 1.$$

If it is assumed that cresol or phenol formation occurs as shown above and that all the other processes involve a NO to NO<sub>2</sub> conversion, then

$$y_{\text{RH}} = y_{\text{PH}} + y_{\text{CR}}$$

This means that  $y_{\text{RR}}$  can be derived given the  $y_{\text{Q2}}$  value that best fits the data and the assigned phenol and cresol yields and the assigned nitrate yield ( $y_{\text{RN}}$ ) parameter.

$$y_{\text{RR}} = 1 - (y_{\text{PH}} + y_{\text{CR}} + y_{\text{Q2}} + y_{\text{RN}}) \quad (\text{XXVI})$$

In addition, we assume that all the ring fragmentation processes, including those that form  $\alpha$ -dicarbonyls, but probably excluding those involving formation of radicals represented by RCO-O2·, involve formation of some type of reactive dicarbonyl product. This implies that

$$\text{Total DCB Yield} = y_{\text{D1}} + y_{\text{D2}} + y_{\text{D3}} = 1 - (y_{\text{Q2}} + y_{\text{NR}} + y_{\text{PH}} + y_{\text{CR}} + y_{\text{BL}} + y_{\text{K6}}) \quad (\text{XXVII})$$

This is used to derive  $y_{\text{D1}}$  given the optimized yields of  $y_{\text{D1}}$ ,  $y_{\text{D3}}$ , and  $y_{\text{Q2}}$  and the assigned yields of the other parameters.

The stoichiometric yield parameters that were assigned or derived for the various aromatic compounds currently incorporated in the mechanism are summarized on Table 42. Footnotes to that table indicating the sources of the derivations are given on Table 43. As indicated in the footnotes, some of the product yield parameters are based on experimental data, some are estimated, and some are adjusted to fit

chamber data. The adjustments were done by using a non-linear optimization method to minimize the sum of squares error between experimental and calculated values of the data indicated on the footnotes, with the errors normalized relative to the maximum values of the measurements for each experiment.

The following points are noted concerning these assignments and the resulting mechanisms for the various types of compounds.

Table 42. Summary of assigned and optimized stoichiometric yield parameters used to represent the reactions of the aromatics.

Parameters and Products	Benzene	Toluene	Ethyl Benzene	o-Xylene	m-Xylene	p-Xylene	
<u>OH abstraction pathway</u>							
yBL BALD		0.085		0.054	0.037	0.083	
yK6 PROD2			0.239				
yNR RO2-N.		0.008	0.024	0.008	0.008	0.008	
Notes	1	6,7	10	6,14	6,14	6,14	
<u>Phenol/Cresol pathway</u>							
yPH PHEN	0.236						
yCR CRES		0.234	0.190	0.161	0.210	0.188	
Notes	2,3	6	11	15	15	15	
<u><math>\alpha</math>-Dicarbonyl products</u>							
yGL GLY	0.207	0.116	0.094	0.084	0.107	0.195	
yMG MGLY		0.135	0.109	0.238	0.335	0.112	
yBA BACL				0.139			
Notes	4,3	8	11,12	8	8	8	
<u>Optimized Fragmentation Products</u>							
yD2 DCB2		0.156		0.060	0.290	0.000	
yD3 DCB3		0.057	0.049	0.145	0.108	0.012	
Notes	5	9	13	16	17	18,19	
<u>Derived Yields [a]</u>							
yRH HO2.	0.236	0.234	0.190	0.161	0.210	0.188	
yRR RO2-R.	0.764	0.758	0.786	0.831	0.782	0.804	
yD1 DCB1	0.764	0.460	0.498	0.572	0.347	0.709	

Parameters and Products	1,2,3-Trimethyl Benzene	1,2,4-Trimethyl Benzene	1,3,5-Trimethyl Benzene	Naphthalene	Methyl Naphthalene	2,3-Dimethyl Naphthalene	Tetralin
<u>OH abstraction pathway</u>							
yBL BALD	0.044	0.044	0.025				
yNR RO2-N.	0.010	0.010	0.010	0.070	0.070	0.070	0.129
Notes [b]	20	20	20	24	29	24	31
<u>Phenol/Cresol pathway</u>							
yPH PHEN				0.236			0.600
yCR CRES	0.186	0.186	0.186		0.236	0.236	
Notes [b]	20	20	20	24	29	24	
<u><math>\alpha</math>-Dicarbonyl products</u>							
yGL GLY	0.065	0.063	0.000	0.084	0.084	0.084	0.084
yMG MGLY	0.166	0.364	0.621		0.038	0.076	
yBA BACL		0.079		25	29	25,30	25
Notes [b]	8	8	8				
<u>Optimized Fragmentation Products</u>							
yD2 DCB2	0.077	0.000	0.097	0.049	0.076	0.103	0.046
yD3 DCB3	0.149	0.027	0.114	0.049	0.076	0.103	0.046
yQ2 RCO-O2.				0.479	0.539	0.600	0.163
Notes [b]	21	22	23	26,27,28	29	26,27,30	26,31
<u>Derived Yields [a]</u>							
yRH HO2.	0.186	0.186	0.186	0.236	0.236	0.236	0.600
yRR RO2-R.	0.804	0.804	0.804	0.215	0.155	0.094	0.108
yD1 DCB1	0.533	0.733	0.569	0.117	0.003	0 [c]	0.016

[a] Parameters calculated using Equations (XXVI) and (XXVII).

[b] Documentation notes are given on Table 42.

[c] Equation (XXVII) predicts a slightly negative DCB1 yield for this compound. Zero yield assumed.

Table 43. Documentation notes for the assigned and optimized stoichiometric yield parameters used to represent the reactions of the aromatics.

No.	Note
1	Organic nitrate yields from reaction of NO to OH - aromatic - O <sub>2</sub> adducts is assumed not to be significant
2	Glyoxal yields from Tuazon et al (1986).
3	See also yield data summarized by Atkinson (1994).
4	Phenol yield from Atkinson et al (1989).
5	Best fits to the D([O <sub>3</sub> ]-[NO]) data in benzene - NO <sub>x</sub> runs ITC560, ITC561, ITC562, ITC710, CTC159A, CTC159B, CTC160A, and CTC160B are obtained if yields of photoreactive DCB products are assumed to be negligible..
6	Aromatic aldehyde and total phenolic product yields are averages of data tabulated by Atkinson (1994), except that the benzaldehyde and tolualdehyde yields of Gery et al (1987) are not used because they are substantially higher than the other measurements.
7	The approximate yield of organic nitrates in the RO <sub>2</sub> +NO reaction are estimated from the benzyl nitrate yields tabulated by Atkinson (1994). Note that this corresponds to an approximately 9.5% yield from benzyl peroxy radicals, which is in the expected range for a molecule of this size.
8	Alpha-dicarbonyl yields are averages of data tabulated by Atkinson (1994), with low values from Shepson et al (1984) and the high values of Tagkagi et al (1980) excluded from the averages.
9	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O <sub>3</sub> ]-[NO]) and toluene in toluene - NO <sub>x</sub> - air runs CTC079, CTC048, CTC026, CTC034, CTC065, DTC042B, DTC155A, DTC151A, DTC170A, and DTC042A.
10	The fraction reacted by abstraction from -CH <sub>2</sub> - group is estimated from the rate constants for ethylbenzene and toluene, and from the benzaldehyde yield from toluene, assuming OH addition to the aromatic ring occurs with the same rate constant as with toluene. The expected abstraction product is benzophenone, which is very approximately represented in the mechanism by the lumped higher oxygenate product PROD2. The organic nitrate yield is estimated to be 10% of reaction of peroxy radical formed after abstraction from the -CH <sub>2</sub> -group. Since abstraction is estimated to occur ~24% of the time and nitrate formation from the OH-aromatic-O <sub>2</sub> adducts is assumed to be negligible, this gives a 2.4% overall nitrate yield.
11	The phenolic product and alpha-dicarbonyl yields, relative to OH addition to aromatic ring, are assumed to be the same as for toluene
12	Methyl glyoxal is used to represent ethyl glyoxal.
13	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O <sub>3</sub> ]-[NO]) and ethylbenzene in ethylbenzene - NO <sub>x</sub> - air runs CTC057, CTC092A, CTC092B, CTC098B, DTC223A, DTC223B, DTC224A, and DTC224B.
14	Nitrate yields for the xylenes are based approximately on the methylbenzyl nitrate yields tabulated by Atkinson (1994). The yields are consistent with 10-20% nitrate formation from reaction of NO with methylbenzyl peroxy radicals.
15	Phenolic product yields from Atkinson et al (1991).
16	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O <sub>3</sub> ]-[NO]) and o-xylene in o-xylene - NO <sub>x</sub> - air runs CTC038, CTC039, CTC046, CTC068, CTC081, CTC091A, DTC207A, DTC207B, DTC208A, DTC208B, DTC209A, and DTC209B.
17	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O <sub>3</sub> ]-[NO]) and m-xylene in m-xylene - NO <sub>x</sub> - air runs CTC029, CTC035, CTC036, CTC094A, DTC193B, DTC192B, DTC206B, DTC295A, DTC188B, and DTC191B.
18	The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O <sub>3</sub> ]-[NO]) and p-xylene in p-xylene - NO <sub>x</sub> - air runs CTC041, CTC043, CTC044, CTC047, CTC070, DTC198A, DTC198B, and DTC199A.



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No. Note

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- 19 Note that the apparent low photoreactive DCB yields from p-xylene and 1,2,4-trimethylbenzene can be attributed to the expected formation of diketone as well as dialdehyde products, where the diketones apparently do not photolyze as rapidly as dialdehydes.
- 20 The extent of reaction via abstraction from CH<sub>3</sub> groups is estimated from average rate constant per CH<sub>3</sub> group derived for toluene and the xylenes, which is  $4.7 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The overall yields of organic nitrates and phenolic products are estimated to be comparable to those for the xylenes, and to be similar for all isomers.
- 21 The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O<sub>3</sub>]-[NO]) and the reactant aromatic in the 1,2,3-trimethylbenzene - NO<sub>x</sub> - air runs CTC054, CTC075, CTC076, DTC211A, DTC211B, DTC212A, DTC212B, DTC213A, and DTC213B.
- 22 The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O<sub>3</sub>]-[NO]) and the reactant aromatic in the 1,2,4-trimethylbenzene - NO<sub>x</sub> - air runs CTC056, CTC091B, CTC093A, CTC093B, DTC201A, DTC201B, DTC203A, DTC203B, DTC204A, and DTC204B.
- 23 The DCB2 and DCB3 yields were adjusted to fit the concentration-time data for D([O<sub>3</sub>]-[NO]) and the reactant aromatic in the 1,3,5-trimethylbenzene - NO<sub>x</sub> - air runs CTC030, CTC050, CTC071, CTC073, DTC194A, DTC194B, DTC195A, DTC195B, DTC196A, DTC196B, and DTC206A.
- 24 The naphthalenes are assumed to have the same yield of phenol-like products as benzene. Abstraction from the methyl group in the methyl naphthalenes is assumed to be relatively unimportant. However, model simulations of naphthalene - NO<sub>x</sub> and 2,3-dimethyl naphthalene runs are best fit by assuming relatively high nitrate yields of 12% and 7%, respectively, though assuming 7% overall yields for both compounds gives satisfactory fits to the data. Note that the actual reactions that this "nitrate formation" parameterization represents may be something other than nitrate formation from peroxy + NO.
- 25 The glyoxal yield from the naphthalenes and tetralin is assumed to be approximately the same as the glyoxal yield from o-xylene.
- 26 Since the only difference between DCB2 and DCB3 is the action spectrum of the photolysis reaction and since the available naphthalene, 2,3-dimethyl naphthalene and tetralin chamber experiments were all carried out using the same light source, the data are not sufficient to determine the yield ratio for these products. Based on the optimization results for the alkylbenzenes, where the optimized DCB2/DCB3 yield ratios varied from 0 to 3 with an average of about 1, we assume that the best fit yields for these two should be roughly equal for the naphthalenes and tetralins.
- 27 Satisfactory fits to the chamber data could not be obtained unless it was assumed that the ring fragmentation process included substantial formation of a peroxyxynitrate precursor, which was represented by the model species RCO-O<sub>2</sub>., the precursor of PAN2. See text.
- 28 The yields of RCO-O<sub>2</sub>. and DCB2 + DCB3 were optimized to fit D([O<sub>3</sub>]-[NO]) data for the naphthalene - NO<sub>x</sub> runs ITC751, ITC755, ITC756, ITC798, and ITC802.
- 29 No chamber data are available to derive a best fit mechanism for this compound. All its mechanistic parameters were derived by averaging those estimated or optimized for naphthalene and 2,3-dimethylnaphthalene.
- 30 The yields of RCO-O<sub>2</sub>. DCB2 + DCB3 and MGLY were optimized to fit D([O<sub>3</sub>]-[NO]) and PAN data for the 2,3-DMN - NO<sub>x</sub> runs ITC771, ITC774, ITC775, and ITC806. Best fits were obtained when the yield of the PAN precursor species was ~0.8, but using a value of 0.6, which is more consistent with the expected upper limit for ring opening, gave similar results. The DCB1 yield calculated using Equation ?? was slightly negative, so a zero DCB1 yield is used.

- 31 Best fits to the chamber data are obtained if relatively high organic nitrate yields and high yields of phenol-like products are assumed. Higher nitrate yields could result if significant abstraction from -CH<sub>2</sub>- groups occurred, forming alkane-like peroxy radicals. It is also necessary to assume some formation of peroxyxynitrate precursors, represented by RCO-O<sub>2</sub>., to obtain satisfactory fits to the data, though the optimum yield for tetralin is less than derived for that for the naphthalenes. The total yield of phenol-like products was set at 0.6, which is reasonably consistent with the maximum value assuming that DCB, nitrate and peroxyxynitrate precursor formation account for the other pathways. The total alkyl nitrate yields, and yields of RCO-O<sub>2</sub>. and DCB<sub>2</sub> + DCB<sub>3</sub> from ring fragmentation were optimized to fit D([O<sub>3</sub>]-[NO]) data for the tetralin - NO<sub>x</sub> runs ITC739, ITC747, ITC748, ITC750, and ITC832.

#### a. Benzene

The glyoxal and phenol yields used were based on experimental data summarized by Atkinson (1997). Contrary to the previous version of the mechanisms (Carter, 1990; Carter et al, 1997a), the data are best fit if it is assumed that the uncharacterized ring fragmentation product does not photolyze to a significant extent. This change can be attributed to the fact that the photoreactivity of glyoxal is increased significantly in the present mechanism. This is based on results of modeling chamber studies of acetylene, where the reactivity of this compound could not be simulated unless significantly higher photoreactivity for glyoxal, its major photoreactive product, is assumed (Carter et al, 1997c; see also footnotes to Table 46 in Table 47). Therefore, only DCB1 is used to represent the uncharacterized fragmentation products from this compound.

Figure 10 shows plots of the  $\Delta([O_3]-[NO])$  data for the benzene - NO<sub>x</sub> experiments that were used for evaluating and deriving the mechanism for this compound. (See Section III for a summary of the model simulation methods and a more complete discussion of the evaluation results for all experiments used.) The results of model simulations using the assigned mechanism are also shown. It can be seen that the mechanism does not perform particularly well in simulating some of the data, tending to overpredict the rate of O<sub>3</sub> formation and NO oxidation in some of the xenon arc chamber runs and significantly underpredicting it in some of the blacklight chamber runs. However, no reasonable alternative parameterization that was examined resulted in a mechanism that better fit the data. Assuming any additional radical source from photolysis of uncharacterized products (or their reaction with O<sub>3</sub> for that matter) exacerbated the overprediction of the reactivity of the xenon arc chamber runs. Assuming higher radicals sources and countering them by increasing termination processes, such as using higher nitrate yield or assuming formation of products represented by PAN precursors (as found to improve simulations of data for the naphthalenes) did not solve the problem. Assuming alternative mechanisms such as formation of radicals that react with NO<sub>2</sub> also did not improve the fits.

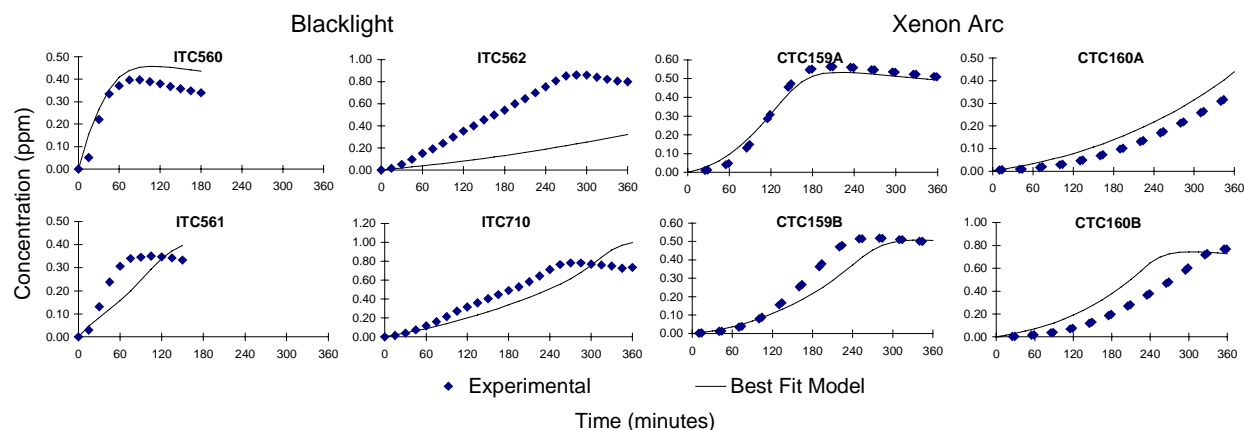


Figure 10. Plots of experimental and calculated  $\Delta([O_3]-[NO])$  data for the experiments used to evaluate the benzene mechanism.

More data are needed concerning the products formed in the photooxidation of benzene and their reactivities, including *direct* studies on the photoreactivity of glyoxal, before the uncertainties in the benzene photooxidation mechanism can be reduced. In addition, the possibility that there are experimental problems with some of the older ITC experiments, where the results appear to be inconsistent, cannot be ruled out. More comprehensive chamber data are needed to more unambiguously evaluate the mechanism for benzene. Although the model performs much better in simulating the data for the alkylbenzenes, and benzene is relatively unimportant in affecting atmospheric  $O_3$  formation (because of its low reactivity and relatively low emissions amounts), the problems with the mechanism for what is presumably the simplest aromatic suggests fundamental problems with all aromatics mechanisms.

### b. Methylbenzenes

The methylbenzenes (toluene, the xylenes and the trimethylbenzenes) are representative of the most important class of aromatic hydrocarbons in terms of both emissions and reactivity, and for that reason have the most extensive database of environmental chamber experiments for mechanism evaluation, as well information concerning yields of known products. The yields of phenolic products, benzaldehyde or tolualdehydes, and the  $\alpha$ -dicarbonyls are based on experimental data summarized by Atkinson (1994). Averages of the reported data were used in those cases where more than one measurement is listed, though in some cases, measurements that appeared to fall outside the distribution of data from other studies were not used when computing the averages. The nitrate yields are somewhat uncertain, but they appear to be relatively low and not highly important in affecting alkylbenzene reactivity.

As discussed above, the yields of model species DCB2 and DCB3, used to represent the uncharacterized photoreactive products, were optimized to fit the chamber data (see the footnotes to Table 42 in Table 43 for the specific data used). As discussed previously (Carter et al, 1997a) it is necessary to assume varying action spectra to fit the data in chambers with different light sources, requiring, and data from chambers with both blacklight and xenon arc light source are needed to determine their yields. Such data are available for all the methylbenzenes through the trimethylbenzenes, permitting their mechanisms to be optimized.

In contrast with benzene, the adjusted mechanism generally performs reasonably well in simulating the available chamber data, with no large or consistent differences in model performance in chambers with differing light sources. The performance of the model in simulating the individual alkylbenzene - NO<sub>x</sub> chamber experiments is similar to that observed with previous versions of the mechanism (Carter et al, 1997a) and is presented in Section III.

### **c. Ethylbenzene**

The mechanism for ethylbenzene is important because it is used as a surrogate (or surrogate species) for all the higher monoalkylbenzenes, such as propylbenzene or cumene. No product data for this compound is given by Atkinson (1994), and thus yields of all products had to be estimated. It is estimated that OH abstraction from the side group is more important than in the case of methylbenzenes because of the more reactive -CH<sub>2</sub>- group, as indicated in the footnotes to Table 42 in Table 43. Other than that, the phenolic and  $\alpha$ -dicarbonyl products are estimated based on those for toluene, reduced by the appropriate factor to correspond to the relatively lower fraction of reaction by OH addition to the aromatic ring.

As with the methylbenzenes, the DCB2 and DCB3 yields were adjusted to optimize the fit of model calculation to the chamber data, which also included experiments with both blacklight and xenon arc light sources. The model fit the data reasonably well (see Section III), performing comparably as the model for the methyl benzenes. However, it is interesting to note that the best fit DCB2 yield for ethylbenzene is zero, while the yield for toluene is relatively high, being larger than that for DCB3 (see Table 42). On the other hand, the DCB3 yields for ethylbenzene and toluene are not greatly different. There is no obvious explanation for the large difference in DCB2 yields, which will have a significant effect on predicted reactivity (see Section ??), and suggests that estimates of comparable reactivity for aromatics with “comparable” structure may not always be reliable.

### **d. Naphthalenes and Tetralin**

Relatively little is known about the details of the atmospheric reactions of naphthalenes and tetralins, except that appears that there are probably significant differences between the mechanisms for the alkylbenzenes and the naphthalenes (e.g., Atkinson, 1999, and references therein). The limited environmental chamber data for these compounds indicate that the naphthalenes and tetralin are considerably less reactive than the alkylbenzenes, despite their relatively high OH rate constants (Carter et al, 1981, 1987). Therefore, it is not appropriate to represent the naphthalenes and tetralins using general aromatic model species, and separate mechanisms are necessary to appropriately predict the reactivities of these compounds.

There was insufficient time and resources in this project to evaluate all available data for the naphthalenes (or tetralins) to determine the most appropriate parameterization for their mechanisms, so the parameterization used for the alkylbenzenes was used as the starting point. The yields of the phenolic products, organic nitrates, and  $\alpha$ -dicarbonyls were very approximately estimated as discussed in the footnotes to Table 42 in Table 43, and optimizations were carried out to determine the best fit DCB2 + DCB3 yields. Because naphthalene and tetralin environmental chamber data are only available with a blacklight light source, it was not possible to separately optimize both products, so their yields were assumed to be the same (see footnotes to the table).

Although adjusting DCB2 and DCB3 yields was found to be sufficient to fit the chamber data for the alkylbenzene runs, this was found not to be the case when attempting to fit the mechanism to

the data for the naphthalenes and tetralins. This is shown, for example, on Figure 11, which shows experimental and calculated  $\Delta([O_3]-[NO])$  data for the naphthalene experiments. The calculated lines labeled “Optimize  $y_{D2}=y_{D3}$ ” show the results of optimizing the photoreactive DCB yields only, using the initial estimates for the other parameters. It can be seen that the  $O_3$  formation and NO oxidation rates in some runs are overpredicted and some are underpredicted, depending on the initial reactant concentrations. The results for 2,3-dimethyl naphthalene and tetralin are similar. In an attempt to improve the fits, a second set of optimizations were carried out where the nitrate yields,  $y_{NR}$ , were optimized along with the photoreactive DCB yields. This also did not result in acceptable fits to the data, as shown on the curves labeled “Optimize  $y_{D2}=y_{D3}, y_{NR}$ ” on Figure 11. Reparameterizing mechanism to represent the possible formation of radicals that react with  $NO_2$  to form termination products (such as phenoxy) and adjusting the yields of those radicals along with the photoreactive DCB yields gives similar results as adjusting the nitrate yields. Using alternative parameterizations where the product yields depend on the absolute  $NO_2$  concentration (as would occur if radicals which react with both  $NO_2$  and  $O_2$  were involved) also did not yield acceptable fits to the data.

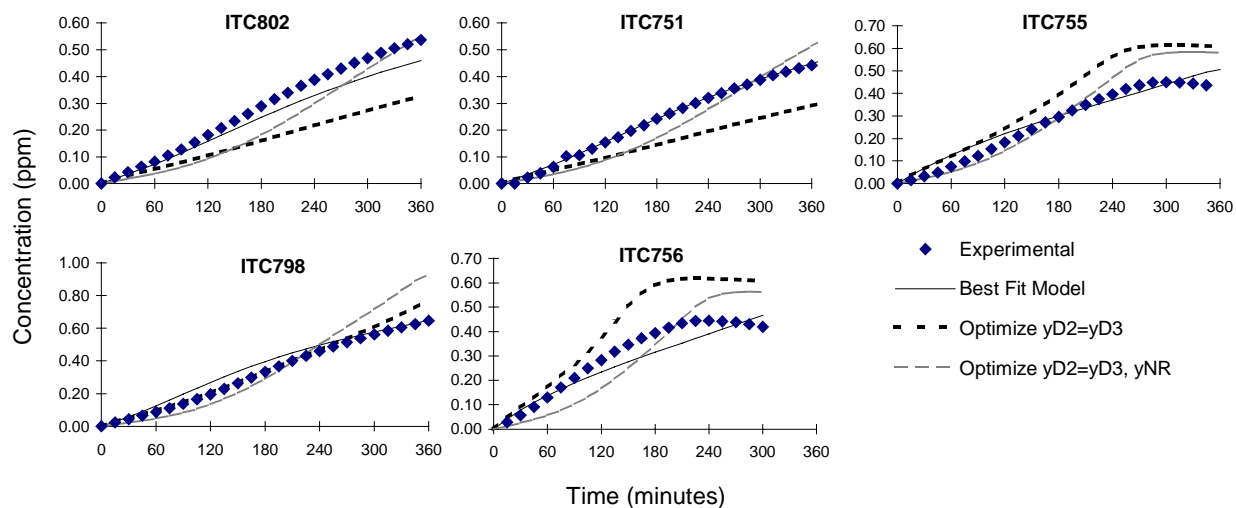


Figure 11. Plots of experimental and calculated  $\Delta([O_3]-[NO])$  data for the naphthalene -  $NO_x$  used to derive the naphthalene mechanism.

Improved fits of the parameterized model to the naphthalene, dimethylnaphthalene, and tetralin data were only obtained when it was assumed that the reactions involved the formation of radicals that in a manner to PAN precursors, which were represented in the model by  $RCO-O_2\cdot$ . The simulations of the naphthalene experiments using the best fit mechanism with the optimized PAN precursor and photoreactive DCB yields given on Table 42 are shown on Figure 11, where it can be seen that reasonably good performance in simulating the data is obtained. The results are similar for 2,3-dimethylnaphthalene and tetralin. However, in the case of 2,3-dimethylnaphthalene the yields of MGLY were also adjusted to optimize fits to the PAN data for these experiments, while for tetralin it was found that it was necessary also to adjust the overall nitrate yield for the model to satisfactorily simulate the data. The higher apparent nitrate yields in the case of tetralin could be due to reactions of radicals formed from OH abstractions from the non-aromatic ring.

These parameterized mechanisms for the naphthalenes and tetralin are clearly highly uncertain. Since the only currently available chamber data came from using a blacklight light source, the mechanism may not be correctly predicting the reactivity contributions of the photoreactive products in sunlight, where the spectrum is more similar to the xenon arc light sources. Perhaps more significantly, if the parameterization employed correspond reasonably well to the underlying chemistry of these compounds, the model may not be correctly extrapolating from the conditions of these experiments to the conditions of the atmosphere. However, these mechanisms represent our current best estimates at the present time.

#### e. Estimated Mechanisms for Other Aromatics

Table 8, above, shows that there are several other aromatic compounds whose OH rate constants are known, but for which no environmental chamber data are available for deriving mechanistic product yield parameters. These compounds are represented in the mechanism with model species using the appropriate measured rate constant, with but product yield parameters that are estimated based on those for most structurally similar compound(s) whose parameters are given in Table 42. These are as follows:

- Chlorobenzene (CL-BEN), dichlorobenzene (CL2-BEN) and nitrobenzene (NO2-BENZ) are assumed to have the same product yield parameters as derived for benzene.
- Parachlorobenzyltrifluoride (PCBTF) and trifluoromethyl benzene (CF3-BEN) are assumed to have the same product yield parameters as derived for toluene.
- Isopropyl benzene (I-C3-BEN), n-propyl benzene (N-C3-BEN) and s-butyl benzene (S-C4-BEN) are assumed to have the same product yield parameters as derived for ethylbenzene.
- Monomethylnaphthalene (ME-NAPH) is assumed to have parameters that are averages of the corresponding parameters for naphthalene and 2,3-dimethylnaphthalene. The parameters so derived are shown on Table 42.

Obviously these estimates are uncertain, especially in view of the differences for the parameters for toluene and ethylbenzene, as discussed above. However, these provide the best available estimates concerning the mechanisms for these compounds, and at least incorporate their known OH rate constants. In this respect, their representation is presumed to be somewhat less uncertain than those aromatics that are not incorporated in the mechanism, but are represented by other aromatics using the “lumped molecule” approach (see Section ??).

## 2. Representation of Terpenes

Terpenes are bicyclic alkenes or dialkenes or cyclic alkenes, and as such their reactions cannot be processed by the current mechanism generation system. The rate constants for their initial reactions are given above in Table 8 (for OH radicals), Table 13 (for NO<sub>3</sub> radicals) Table 16 (for O<sub>3</sub>) and Table 22 (for O<sup>3</sup>P atoms). Although some product data are available for their reactions with OH radicals and O<sub>3</sub> (see Atkinson, 1997a), the available information is not sufficient to completely determine their mechanisms. Their representation is therefore estimated based on simplified or parameterized mechanisms, or using mechanisms generated for similar monocyclic, monoalkene structures.

The terpenes whose reactions are represented in this mechanism are  $\alpha$ - and  $\beta$ -pinenes,  $\Delta^3$ -carene, d-limonene, and sabinene, the only terpenes for which environmental chamber data are available. The mechanisms used for these compounds, given in terms of model species in the base mechanism, are given in Table 44. The considerations used when deriving mechanisms for the terpenes are discussed below. The performance of these mechanisms in simulating the chamber data for these compounds is summarized in Section ??.

Table 44. Assigned mechanisms for terpenes and other non-aromatic compounds or groups of compounds that are not processed using the mechanism generation system.

A	Ea	Reaction
<u><math>\alpha</math>-Pinene</u>		
1.21e-11	-0.882	A-PINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.5 XC
1.01e-15	1.455	A-PINENE + O3 = #.7 HO. + #.081 RO2-R. + #.321 RO2-N. + #1.375 R2O2. + #.298 RCO-O2. + #.051 CO + #.339 HCHO + #.218 RCHO + #.345 ACET + #.002 GLY + #.081 BACL + #.3 RCO-OH + #3.875 XC
1.19e-12	-0.974	A-PINENE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
3.20e-11		A-PINENE + O3P = PROD2 + #4 XC
<u><math>\beta</math>-Pinene</u>		
2.38e-11	-0.709	B-PINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 HCHO + #.75 PROD2 + #3.25 XC
1.01e-15	2.493	B-PINENE + O3 = #.34 HO. + #.09 HO2. + #.05 RO2-N. + #.2 R2O2. + #.2 RCO-O2. + #.375 CO + #.1 CO2 + #.25 HCHO + #.75 PROD2 + #.28 HCOOH + #3.595 XC
2.51e-12		B-PINENE + NO3 = #.75 RO2-R. + #.25 RO2-N. + #.75 R2O2. + #.75 RNO3 + #4 XC + #.25 XN
2.70e-11		B-PINENE + O3P = #.4 RCHO + #.6 PROD2 + #5.2 XC
<u><math>\Delta^3</math> Carene</u>		
1.64e-11	-0.994	3-CARENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.25 XC
1.01e-15	1.958	3-CARENE + O3 = #.7 HO. + #.161 RO2-N. + #.539 R2O2. + #.482 CCO-O2. + #.058 RCO-O2. + #.058 HCHO + #.482 RCHO + #.3 RCO-OH + #5.492 XC
9.10e-12		3-CARENE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
3.20e-11		3-CARENE + O3P = PROD2 + #4 XC
<u>Sabinene</u>		
2.19e-11	-0.994	SABINENE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 HCHO + #.75 PROD2 + #3.25 XC
1.01e-15	1.459	SABINENE + O3 = #.34 HO. + #.09 HO2. + #.05 RO2-N. + #.2 R2O2. + #.2 RCO-O2. + #.375 CO + #.1 CO2 + #.25 HCHO + #.75 PROD2 + #.28 HCOOH + #3.595 XC
1.00e-11		SABINENE + NO3 = #.75 RO2-R. + #.25 RO2-N. + #.75 R2O2. + #.75 RNO3 + #4 XC + #.25 XN
1.69e-11		SABINENE + O3P = #.4 RCHO + #.6 PROD2 + #5.2 XC
<u>D-Limonene</u>		
3.19e-11	-0.994	D-LIMONE + HO. = #.75 RO2-R. + #.25 RO2-N. + #.5 R2O2. + #.75 RCHO + #6.25 XC
3.71e-15	1.729	D-LIMONE + O3 = #.7 HO. + #.161 RO2-N. + #.539 R2O2. + #.482 CCO-O2. + #.058 RCO-O2. + #.058 HCHO + #.482 RCHO + #.3 RCO-OH + #5.492 XC
1.22e-11		D-LIMONE + NO3 = #.75 NO2 + #.25 RO2-N. + #.75 R2O2. + #.75 RCHO + #6.25 XC + #.25 XN
7.20e-11		D-LIMONE + O3P = PROD2 + #4 XC
<u>Styrene</u>		
5.80e-11		STYRENE + HO. = #.87 RO2-R. + #.13 RO2-N. + #.87 HCHO + #.87 BALD + #.26 XC
1.71e-17		STYRENE + O3 = #.4 HCHO + #.6 BALD + #.6 HCOOH + #.4 RCO-OH + #1.6 XC
1.51e-13		STYRENE + NO3 = #.22 NO2 + #.65 RO2-R. + #.13 RO2-N. + #.22 R2O2. + #.22 HCHO + #.22 BALD + #.65 RNO3 + #1.56 XC + #.13 XN
1.76e-11		STYRENE + O3P = PROD2 + #2 XC
<u>N-Methyl-2-Pyrrolidone</u>		
2.15e-11		NMP + HO. = #.92 HO2. + #.08 RO2-N. + #.46 RCHO + #.46 PROD2 + #.38 XC + XN
1.26e-13		NMP + NO3 = #.92 HO2. + #.08 RO2-N. + HNO3 + #.92 PROD2 + #1 XC + XN

Notes:

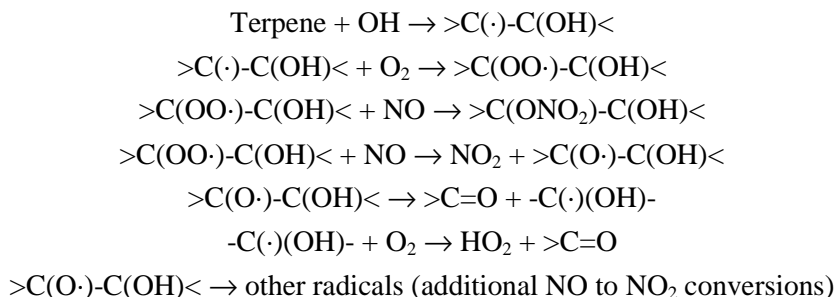
A factor in  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ ; activation energy in kcal/mole.

See text for a discussion of how the mechanisms were derived.



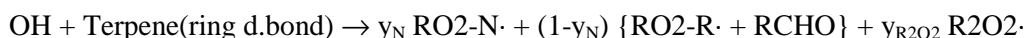
### a. Reaction with OH radicals

In the case of the reaction with OH radicals, the simplest mechanism would involve OH adding to the double bond, forming a  $\beta$ -hydroxy radical which will react with  $O_2$  to form the corresponding peroxy radical, which reacts with NO to form either the corresponding nitrate or alkoxy radical, and where the alkoxy radical can react in various ways, including decomposing to ultimately forming  $HO_2$  and carbonyl compounds.

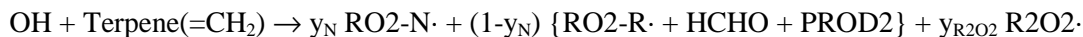


If the decomposition involves breaking what was the double bond to form an  $\alpha$ -hydroxy radical, which is the dominant process for most of the simpler alkenes, then no additional NO to  $\text{NO}_2$  conversions would be involved. However, additional NO to  $\text{NO}_2$  conversions may occur if other decompositions can compete, which are estimated to be non-negligible for compounds with similar structures as the terpenes. If the reacting double bond is in the ring, the carbonyl products would be expected to be bifunctional compounds with at least one aldehyde group, which is represented in the model by the RCHO model species. If the reacting double bond is a  $=\text{CH}_2$  group outside the ring, then the products would be formaldehyde + a ketone, the latter represented by PROD2 in the model.

Therefore, for compounds with the double bond in the ring, such as  $\alpha$ -pinene,  $\Delta^3$ -carene, and d-limonene, the following parameterized mechanism is employed:



where the nitrate yield,  $y_N$ , and the amount of extra NO to  $\text{NO}_2$  conversions,  $y_{\text{R2O}_2}$ , are determined based on model simulations of the available terpene -  $\text{NO}_x$  chamber data. For compounds with  $=\text{CH}_2$  groups, such as  $\beta$ -pinene and sabinene, the parameterized mechanism is



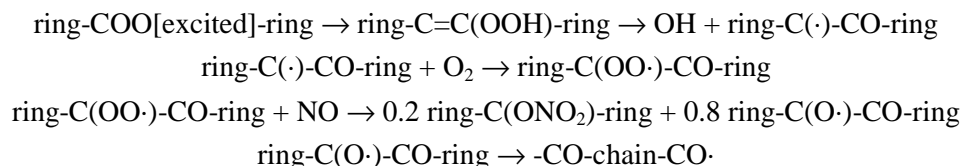
Best fits to most of the chamber data are obtained using  $y_N = 0.25$  and  $y_{\text{R2O}_2} = 0.5$ , and as indicated on Table 44 this is assumed for all the terpenes.

### b. Reaction with $O_3$

The Crigee biradicals expected to be formed in the reactions of  $O_3$  with  $\alpha$ -pinene,  $\Delta^3$ -carene and d-limonene could all be represented in the mechanism generation system, so the overall  $O_3$  reactions could be generated in the same way as used for the other alkenes, if the mechanism for the initial reaction is assigned. This is the approach used for these compounds. All three of these compounds have trisubstituted double bond in the ring, and as discussed above in Section II.B.5.c, it is assumed that the formation of  $\text{-CO-}$  +  $\text{-CHOO[excited]}$  and  $\text{-CHO}$  +  $\text{-COO[excited]}$  occur respectively 30% and 70% of the time, based on ketone yields from acyclic trisubstituted alkenes. Although d-limonene has a second

double bond outside the ring, it is assumed that most of the reaction occurs at the more substituted bond in the ring, and reactions at the second double bond is ignored when estimating the overall mechanism. Note that this procedure results in predicted OH yields of 70% for these compounds, which is reasonably close to the experimentally-determined values of 0.76-0.85 for  $\alpha$ -pinene and 86% for d-limonene (Atkinson, 1997b). The overall processes generated in this way are shown in Table 44.

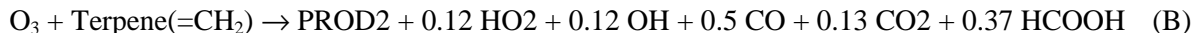
The mechanism generation system cannot be used as readily to estimate the reactions of  $O_3$  with  $\beta$ -pinene and sabinene, since reaction to form formaldehyde + a Crigiee biradical with a bicyclic structure is expected to be formed to a non-negligible extent. However, the expected overall reactions of these biradicals are not expected to differ greatly with the structure, at least in terms of model species in the base mechanism. This is expected to be as follows,



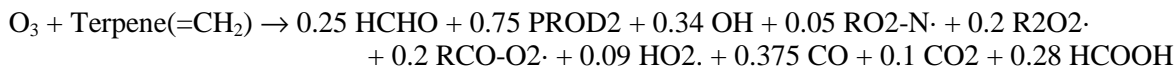
where the 20% nitrate yield is the value derived by the mechanism generation system for a substituted  $C_9$  peroxy radical, such as expected to be formed in this case. Therefore, in terms of model species in the base mechanism, reaction of the terpene with  $O_3$  to form this biradical yields the following overall process:



Of course, part of the time the reaction would also involve formation of the cyclic ketone +  $\text{HCHO}_2\text{[excited]}$ , whose subsequent reactions are as discussed above. In this case, the overall process is



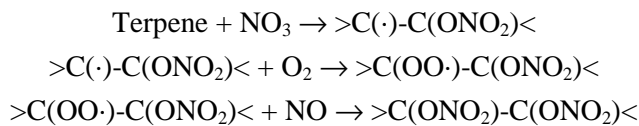
The branching ratio for these two routes is derived based on assuming an overall OH yield of ~35%, which is the measured value for  $\beta$ -pinene and close to the measured values of 26% and 33% for sabinene (Atkinson, 1997a and references therein). This is predicted if Pathways (A) and (B) are assumed to occur respectively 25% and 75% of the time, which gives the following overall process:

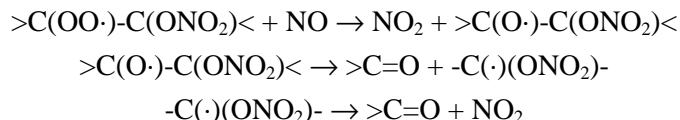


Note, however, that assuming ~75% ketone +  $\text{HCHO}_2\text{[excited]}$  formation is not consistent with the observed yields of only 22-23% nopinone from  $\beta$ -pinene and 50% ketone from sabinene (Atkinson, 1997a, and references therein), so this is clearly an oversimplification of the actual mechanisms for these terpenes.

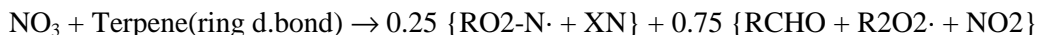
### c. Reaction with $\text{NO}_3$ Radicals

The mechanisms for the terpene +  $\text{NO}_3$  reactions are represented in a manner similar to that used for the OH reactions as discussed above, being based on assuming the following set of reactions:





The alkoxy radical estimation methods discussed above predict that the  $>\text{C}(\text{O}\cdot)\text{-C}(\text{ONO}_2)<$  radicals of the types formed in these reactions should primarily decompose, so the possible competing reactions are not considered. As with the OH reaction, the carbonyls formed would either be a bifunctional aldehyde (represented by the RCHO model species) in the case of terpenes with double bonds in the ring, or formaldehyde + a ketone (represented by PROD2) in the case of terpenes with  $=\text{CH}_2$  groups. If the same overall nitrate yield is assumed as is used in the OH reaction (~25%), then the overall process is:



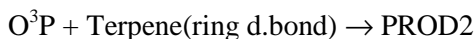
for terpenes with the double bond in the ring, and



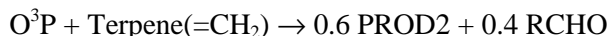
for terpenes with  $=\text{CH}_2$  groups.

#### d. Reaction with $\text{O}^3\text{P}$

As discussed above in Section II.B.6.c, it is assumed that the reactions of  $\text{O}^3\text{P}$  with the higher alkenes involve formation of ~60% of the corresponding oxide, and ~40% formation of a carbonyl compound. The oxide formed in the reactions of  $\text{O}^3\text{P}$  with the terpenes are represented by the PROD2 model species. For terpenes with the double bond in the ring, the carbonyl product is expected to be primarily a ketone, which is also represented in the model by PROD2, while if the terpene has a  $=\text{CH}_2$  group, the predicted product is an aldehyde, whose formation is represented by RCHO. Thus, the overall reactions are



for terpenes with the double bond in the ring, and



for terpenes with  $=\text{CH}_2$  groups.

### 3. Representation of Other Compounds

Table 44 shows the representation used for the reactions of several other compounds or classes of compounds that are incorporated in the present mechanism and that do not fall into the categories discussed above. The sources of the assignments are discussed below.

#### a. Styrene

The mechanism used for the reactions of styrene is based on that derived by Carter et al (1999c) based on environmental chamber experiments employing that compound. Note that to fit the environmental chamber reactivity data it is necessary to assume that essentially no radical formation occurs in the  $\text{O}_3$  reaction. The only modification to the mechanism of Carter et al (1999c) is that the nitrate yield for the OH reaction was increased from 10% to 13% to reduce biases in the model

simulations of the mini-surrogate incremental reactivity experiments. The nitrate yield in the NO<sub>3</sub> reaction was also increased from 10% to 13%, since it is assumed to be the same in the OH reaction.

#### **b. N-Methyl-2-Pyrrolidone**

The mechanism for the reactions of N-methyl-2-pyrrolidone (NMP) is based on that derived by Carter et al (1996c), based on environmental chamber experiments employing that compound. The main differences are that the products 1-formyl-2-pyrrolidinone and N-methyl succinimide were represented by PROD2 and RCHO, respectively, rather than by separate model species with parameterized mechanisms. In addition, the nitrate yields used in the mechanism had to be reduced from 15% to 8% for the model to give reasonably good simulations of the data. The fits of the model simulations to the chamber data are given in Section ??.

#### **c. Halogenated Compounds**

The reactions of halogenated compound are not represented in the current version of the mechanism. Although we have previously carried out experimental studies of the ozone reactivities of chloropicrin (CCl<sub>3</sub>ONO<sub>2</sub>) (Carter et al, 1997h), n-propyl and n-butyl bromides (Carter et al, 1997d) and trichloroethylene (Carter et al, 1996d), and developed mechanisms for those compounds to be evaluated using the data obtained, satisfactory fits of the model to chamber data were obtained only for chloropicrin. In particular, no reasonable adjustments of uncertain portions of the mechanisms would result in satisfactory fits to the data for the alkyl bromides (Carter et al, 1997d) or trichloroethylene (Carter et al, 1996d), especially after the times in the experiment when O<sub>3</sub> formation began. Additional data are needed, with chemically simpler systems, before mechanisms can be developed that can reliably predict ozone impacts of halogenated compounds.

#### **d. Other Compounds**

Although Table 8 includes OH radical rate constants for the atmospheric reactions of representatives of other classes of organic compounds, including several amines and some sulfur- and silicon-containing compounds, these are not represented in the current version of the mechanism. With the exception of Toluene diisocyanate (TDI) (Carter et al, 1997i) and several volatile siloxanes (Carter et al, 1992), which were shown to be ozone inhibitors under all conditions, there is insufficient data available to develop mechanisms for these compounds. Although highly approximate estimated mechanisms could be developed in some cases, there was insufficient time and resources available to carry this out for this version of the mechanism.

### **D. Detailed Model Species**

#### **1. Listing and Summary of Detailed Model Species**



Most of the emitted VOCs are represented in the model using “detailed model species” (DMS), which can represent either individual compounds or classes of isomeric compounds that are represented as having the same overall mechanism. These are a superset of the “explicit model species” discussed above (and listed in Table 45). In addition to the explicit model species, which always be explicitly incorporated in the model to represent the reactive products, while the DMS include species that can either be included, excluded, or lumped with other DMS, depending in the model application. Some of these DMS have explicit mechanisms assigned to them, which can be given either as reactions to be incorporated into the model for explicit representation of the VOC(s) it represents, or as kinetic and

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Reference for expanded Carbon Bond IV

## **V. APPENDIX A: MECHANISM LISTING AND TABULATIONS**

Table 45. Listing of model species used in the base mechanism

Type and Name	Description
<u>Constant Species.</u>	
O2	Oxygen
M	Air
H2O	Water
HV	Light
<u>Active Inorganic Species.</u>	
O3	Ozone
NO	Nitric Oxide
NO2	Nitrogen Dioxide
NO3	Nitrate Radical
N2O5	Nitrogen Pentoxide
HONO	Nitrous Acid
HNO3	Nitric Acid
HNO4	Peroxynitric Acid
HO2H	Hydrogen Peroxide
CO	Carbon Monoxide
SO2	Sulfur Dioxide
<u>Active Radical Species and Operators.</u>	
HO.	Hydroxyl Radicals
HO2.	Hydroperoxide Radicals
C-O2.	Methyl Peroxy Radicals
RO2-R.	Peroxy Radical Operator representing NO to NO2 conversion with HO2 formation.
R2O2.	Peroxy Radical Operator representing NO to NO2 conversion without HO2 formation.
RO2-N.	Peroxy Radical Operator representing NO consumption with organic nitrate formation.
CCO-O2.	Acetyl Peroxy Radicals
RCO-O2.	Peroxy Propionyl and higher peroxy acyl Radicals
BZCO-O2.	Peroxyacyl radical formed from Aromatic Aldehydes
MA-RCO3.	Peroxyacyl radicals formed from methacrolein and other acroleins.
<u>Steady State Radical Species</u>	
O3P	Ground State Oxygen Atoms
O*1D2	Excited Oxygen Atoms
TBU-O.	t-Butoxy Radicals
BZ-O.	Phenoxy Radicals
BZ(NO2)-O.	Nitro-substituted Phenoxy Radical
HOCOO.	Radical formed when Formaldehyde reacts with HO2
<u>PAN and PAN Analogues</u>	
PAN	Peroxy Acetyl Nitrate
PAN2	PPN and other higher alkyl PAN analogues
PBZN	PAN analogues formed from Aromatic Aldehydes
MA-PAN	PAN analogue formed from Methacrolein
<u>Explicit and Lumped Molecule Reactive Organic Product Species</u>	
HCHO	Formaldehyde
CCHO	Acetaldehyde
RCHO	Lumped C3+ Aldehydes

Table 45 (continued)

Type and Name	Description
ACET	Acetone
MEK	Ketones and other non-aldehyde oxygenated products which react with OH radicals slower than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$ .
MEOH	Methanol
COOH	Methyl Hydroperoxide
ROOH	Lumped higher organic hydroperoxides
GLY	Glyoxal
MGLY	Methyl Glyoxal
BACL	Biacetyl
PHEN	Phenol
CRES	Cresols
NPHE	Nitrophenols
BALD	Aromatic aldehydes (e.g., benzaldehyde)
METHACRO	Methacrolein
MVK	Methyl Vinyl Ketone
ISOPROD	Lumped isoprene product species
<u>Lumped Parameter Products</u>	
PROD2	Ketones and other non-aldehyde oxygenated products which react with OH radicals faster than $5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ sec}^{-1}$ .
RNO3	Lumped Organic Nitrates
<u>Uncharacterized Reactive Aromatic Ring Fragmentation Products</u>	
DCB1	Reactive Aromatic Fragmentation Products that do not undergo significant photodecomposition to radicals.
DCB2	Reactive Aromatic Fragmentation Products which photolyze with alpha-dicarbonyl-like action spectrum.
DCB3	Reactive Aromatic Fragmentation Products which photolyze with acrolein action spectrum.
<u>Non-Reacting Species</u>	
CO2	Carbon Dioxide
XC	Lost Carbon
XN	Lost Nitrogen
SULF	Sulfates ( $\text{SO}_3$ or $\text{H}_2\text{SO}_4$ )
<u>Low Reactivity Compounds or Unknown Products Represented as Unreactive</u>	
H2	Hydrogen
HCOOH	Formic Acid
CCO-OH	Acetic Acid
RCO-OH	Higher organic acids
CCO-OOH	Peroxy Acetic Acid
RCO-OOH	Higher organic peroxy acids
CONO2	Methyl Nitrate
NROG	Unspecified Unreactive Carbon
<u>Primary Organics Represented explicitly</u>	
CH4	Methane

Table 46. Listing and documentation of the reactions in the base mechanism.

Label	Rate Parameters [a]				Refs & Notes	Reaction and Products [b]
	k(298)	A	Ea	B		
<u>Inorganic Reactions</u>						
1		Phot Set= NO2			1,2	NO2 + HV = NO + O3P
2	5.79e-34	5.68e-34	0.00	-2.8	3	O3P + O2 + M = O3 + M
3	7.96e-15	8.00e-12	4.09		4,5	O3P + O3 = #2 O2
4	1.01e-31	1.00e-31	0.00	-1.6	6,7,5	O3P + NO + M = NO2 + M
5	9.72e-12	6.50e-12	-0.24		4,5	O3P + NO2 = NO + O2
6	1.82e-12	Falloff, F=0.80			4,7,5,7a	O3P + NO2 = NO3 + M
	0:	9.00e-32	0.00	-2.0		
	inf:	2.20e-11	0.00	0.0		
8	1.81e-14	1.80e-12	2.72		6	O3 + NO = NO2 + O2
9	3.52e-17	1.40e-13	4.91		6	O3 + NO2 = O2 + NO3
10	2.60e-11	1.80e-11	-0.22		6	NO + NO3 = #2 NO2
11	1.95e-38	3.30e-39	-1.05		6	NO + NO + O2 = #2 NO2
12	1.54e-12	Falloff, F=0.45			6,7	NO2 + NO3 = N2O5
	0:	2.80e-30	0.00	-3.5		
	inf:	2.00e-12	0.00	0.2		
13	5.28e-2	Falloff, F=0.45			6,7	N2O5 = NO2 + NO3
	0:	1.00e-3	21.86	-3.5		
	inf:	9.70e+14	22.02	0.1		
14	2.60e-22	2.60e-22			8	N2O5 + H2O = #2 HNO3
15		(Slow)			9	N2O5 + HV = NO3 + NO + O3P
16		(Slow)			9	N2O5 + HV = NO3 + NO2
17	6.56e-16	4.50e-14	2.50		10	NO2 + NO3 = NO + NO2 + O2
18		Phot Set= NO3NO			1,11,12	NO3 + HV = NO + O2
19		Phot Set= NO3NO2			1,11,12	NO3 + HV = NO2 + O3P
20		Phot Set= O3O3P			1,13,14	O3 + HV = O3P + O2
21		Phot Set= O3O1D			1,13,14	O3 + HV = O*1D2 + O2
22	2.20e-10	2.20e-10			4	O*1D2 + H2O = #2 HO.
23	2.87e-11	2.09e-11	-0.19		15	O*1D2 + M = O3P + M
24	7.41e-12	Falloff, F=0.60			16	HO. + NO = HONO
	0:	7.00e-31	0.00	-2.6		
	inf:	3.60e-11	0.00	-0.1		
25		Phot Set= HONO-NO			1,17,18	HONO + HV = HO. + NO
26		Phot Set= HONO-NO2			1,17,18	HONO + HV = HO2. + NO2
27	6.46e-12	2.70e-12	-0.52		6	HO. + HONO = H2O + NO2
28	8.98e-12	Falloff, F=0.60			19	HO. + NO2 = HNO3
	0:	2.43e-30	0.00	-3.1		
	inf:	1.67e-11	0.00	-2.1		
29	2.00e-11	2.00e-11			6,20	HO. + NO3 = HO2. + NO2
30	1.47e-13	k = k0+k3M/(1+k3M/k2)			21,22	HO. + HNO3 = H2O + NO3
	k0:	7.20e-15	-1.56	0.0		
	k2:	4.10e-16	-2.86	0.0		
	k3:	1.90e-33	-1.44	0.0		
31		Phot Set= HNO3			1,23	HNO3 + HV = HO. + NO2

Table 46 (continued)

Label	Rate Parameters [a]				Refs & Notes	Reaction and Products [b]
	k(0)	A	Ea	B		
32	2.09e-13	k = k1 + k2 [M]			24	HO. + CO = HO2. + CO2
	k1:	1.30e-13	0.00	0.0		
	k2:	3.19e-33	0.00	0.0		
33	6.63e-14	1.90e-12	1.99		6	HO. + O3 = HO2. + O2
34	8.41e-12	3.40e-12	-0.54		6	HO2. + NO = HO. + NO2
35	1.38e-12	Falloff, F=0.60			6	HO2. + NO2 = HNO4
	0:	1.80e-31	0.00	-3.2		
	inf:	4.70e-12	0.00	0.0		
36	7.55e-2	Falloff, F=0.50			6	HNO4 = HO2. + NO2
	0:	4.10e-5	21.16	0.0		
	inf:	5.70e+15	22.20	0.0		
37	Phot Set= HO2NO2				1,25	HNO4 + HV = #.61 {HO2. + NO2} + #.39 {HO. + NO3}
38	5.02e-12	1.50e-12	-0.72		6	HNO4 + HO. = H2O + NO2 + O2
39	1.87e-15	1.40e-14	1.19		6	HO2. + O3 = HO. + #2 O2
40A	2.87e-12	k = k1 + k2 [M]			26	HO2. + HO2. = HO2H + O2
	k1:	2.20e-13	-1.19	0.0		
	k2:	1.85e-33	-1.95	0.0		
40B	6.46e-30	k = k1 + k2 [M]			26	HO2. + HO2. + H2O = HO2H + O2 + H2O
	k1:	3.08e-34	-5.56	0.0		
	k2:	2.59e-54	-6.32	0.0		
41	4.00e-12	4.00e-12			27	NO3 + HO2. = #.8 {HO. + NO2 + O2} + #.2 {HNO3 + O2}
42	2.28e-16	8.50e-13	4.87		28	NO3 + NO3 = #2 NO2 + O2
43	Phot Set= H2O2				1,29	HO2H + HV = #2 HO.
44	1.70e-12	2.90e-12	0.32		6	HO2H + HO. = HO2. + H2O
45	1.11e-10	4.80e-11	-0.50		6	HO. + HO2. = H2O + O2
S2OH	4.09e-31	Falloff, F=0.45			6,30	HO. + SO2 = HO2. + SULF
	0:	2.00e-12	0.00	0.0		
	inf:	4.00e-31	0.00	-3.3		
<u>Methyl peroxy and methoxy reactions</u>						
MER1	7.29e-12	2.80e-12	-0.57		31,32	C-O2. + NO = NO2 + HCHO + HO2.
MER4	5.21e-12	3.80e-13	-1.55		31	C-O2. + HO2. = COOH + O2
MEN3	1.30e-12	1.30e-12			31	C-O2. + NO3 = HCHO + HO2. + NO2
MER5	2.65e-13	2.45e-14	-1.41		33	C-O2. + C-O2. = MEOH + HCHO + O2
MER6	1.07e-13	5.90e-13	1.01		33	C-O2. + C-O2. = #2 {HCHO + HO2.}
<u>Peroxy Radical Operators</u>						
RRNO	9.04e-12	2.70e-12	-0.72		34,35,32	RO2-R. + NO = NO2 + HO2.
RRH2	1.49e-11	1.90e-13	-2.58		35,36	RO2-R. + HO2. = ROOH + O2 + #-3 XC
RRN3	2.30e-12	2.30e-12			37,38	RO2-R. + NO3 = NO2 + O2 + HO2.
RRME	2.00e-13	2.00e-13			39,40	RO2-R. + C-O2. = HO2. + #.75 HCHO + #.25 MEOH
RRR2	3.50e-14	3.50e-14			41,40	RO2-R. + RO2-R. = HO2.
R2NO	Same k as rxn RRNO				42,43	R2O2. + NO = NO2
R2H2	Same k as rxn RRH2				42,43	R2O2. + HO2. = HO2.
R2N3	Same k as rxn RRN3				42,43	R2O2. + NO3 = NO2
R2ME	Same k as rxn RRME				42,43	R2O2. + C-O2. = C-O2.

Table 46 (continued)

Label	Rate Parameters [a]				Refs &	Reaction and Products [b]
	k(0)	A	Ea	B	Notes	
R2RR	Same k as rxn RRR2				42,43,40	R2O2. + RO2-R. = RO2-R.
R2R3	Same k as rxn RRR2				42,43	R2O2. + R2O2. =
RNNO	Same k as rxn RRNO				42,44	RO2-N. + NO = RNO3
RNH2	Same k as rxn RRH2				42,44,45	RO2-N. + HO2. = ROOH + #3 XC
RNME	Same k as rxn RRME				42,44,46	RO2-N. + C-O2. = HO2. + #.25 MEOH + #.5 {MEK + PROD2} + #.75 HCHO + XC
RNN3	Same k as rxn RRN3				42,44,47	RO2-N. + NO3 = NO2 + O2 + HO2. + MEK + #2 XC
RNRR	Same k as rxn RRR2				42,44,46	RO2-N. + RO2-R. = HO2. + #.5 {MEK + PROD2} + O2 + XC
RNR2	Same k as rxn RRR2				42,43	RO2-N. + R2O2. = RO2-N.
RNRN	Same k as rxn RRR2				42,44,46	RO2-N. + RO2-N. = MEK + HO2. + PROD2 + O2 + #2 XC
<u>Reactions of Acyl Peroxy Radicals, PAN, and PAN analogues</u>						
APN2	1.05e-11	Falloff, F=0.30			48	CCO-O2. + NO2 = PAN
	0:	2.70e-28	0.00	-7.1		
	inf:	1.20e-11	0.00	-0.9		
DPAN	5.21e-4	Falloff, F=0.30			49	PAN = CCO-O2. + NO2
	0:	4.90e-3	24.05	0.0		
	inf:	4.00e+16	27.03	0.0		
APNO	2.13e-11	7.80e-12	-0.60		50	CCO-O2. + NO = C-O2. + CO2 + NO2
APH2	1.41e-11	4.30e-13	-2.07		51	CCO-O2. + HO2. = #.75 {CCO-OOH +O2} + #.25 {CCO-OH + O3}
APN3	4.00e-12	4.00e-12			52	CCO-O2. + NO3 = C-O2. + CO2 + NO2 + O2
APME	9.64e-12	1.80e-12	-0.99		53	CCO-O2. + C-O2. = CCO-OH + HCHO + O2
APRR	7.50e-12	7.50e-12			54,55	CCO-O2. + RO2-R. = CCO-OH
APR2	Same k as rxn APRR				42,43	CCO-O2. + R2O2. = CCO-O2.
APRN	Same k as rxn APRR				42,55,46	CCO-O2. + RO2-N. = CCO-OH + PROD2
APAP	1.55e-11	2.90e-12	-0.99		31	CCO-O2. + CCO-O2. = #2 {C-O2. + CO2} + O2
PPN2	1.21e-11	1.20e-11	0.00	-0.9	56,57	RCO-O2. + NO2 = PAN2
PAN2	4.43e-4	2.00e+15	25.44		58,57	PAN2 = RCO-O2. + NO2
PPNO	2.80e-11	1.25e-11	-0.48		58a,57	RCO-O2. + NO = NO2 + CCHO + RO2-R. + CO2
PPH2	Same k as rxn APH2				59,57	RCO-O2. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3}
PPN3	Same k as rxn APN3				59,57	RCO-O2. + NO3 = NO2 + CCHO + RO2-R. + CO2 + O2
PPME	Same k as rxn APME				59,57	RCO-O2. + C-O2. = RCO-OH + HCHO + O2
PPRR	Same k as rxn APRR				59,57	RCO-O2. + RO2-R. = RCO-OH + O2
PPR2	Same k as rxn APRR				59,43	RCO-O2. + R2O2. = RCO-O2.
PPRN	Same k as rxn APRR				59,46,57	RCO-O2. + RO2-N. = RCO-OH + PROD2 + O2
PPAP	Same k as rxn APAP				59,57	RCO-O2. + CCO-O2. = #2 CO2 + C-O2. + CCHO + RO2-R. + O2
PPPP	Same k as rxn APAP				59,57	RCO-O2. + RCO-O2. = #2 {CCHO + RO2-R. + CO2}
BPN2	1.37e-11	1.37e-11			60	BZCO-O2. + NO2 = PBZN
BPAN	3.12e-4	7.90e+16	27.82		61	PBZN = BZCO-O2. + NO2
BPNO	Same k as rxn PPNO				62,63	BZCO-O2. + NO = NO2 + CO2 + BZ-O. + R2O2.

Table 46 (continued)

Label	Rate Parameters [a]			B	Refs & Notes	Reaction and Products [b]
	k(0)	A	Ea			
BPH2	Same k as rxn APH2				62,63	BZCO-O2. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3} + #4 XC
BPN3	Same k as rxn APN3				62,63	BZCO-O2. + NO3 = NO2 + CO2 + BZ-O. + R2O2. + O2
BPME	Same k as rxn APME				62,63	BZCO-O2. + C-O2. = RCO-OH + HCHO + O2 + #4 XC
BPRR	Same k as rxn APRR				62,63	BZCO-O2. + RO2-R. = RCO-OH + O2 + #4 XC
BPR2	Same k as rxn APRR				43,62	BZCO-O2. + R2O2. = BZCO-O2.
BPRN	Same k as rxn APRR				46,62,63	BZCO-O2. + RO2-N. = RCO-OH + PROD2 + O2 + #4 XC
BPAP	Same k as rxn APAP				62,63	BZCO-O2. + CCO-O2. = #2 CO2 + C-O2. + BZ-O. + R2O2.
BPPP	Same k as rxn APAP				62,57,63	BZCO-O2. + RCO-O2. = #2 CO2 + CCHO + RO2-R. + BZ-O. + R2O2.
BPBP	Same k as rxn APAP				62,63	BZCO-O2. + BZCO-O2. = #2 {BZ-O. + R2O2. + CO2}
MPN2	Same k as rxn PPN2				62,64	MA-RCO3. + NO2 = MA-PAN
MPPN	3.55e-4	1.60e+16	26.80		65	MA-PAN = MA-RCO3. + NO2
MPNO	Same k as rxn PPNO				62,64	MA-RCO3. + NO = NO2 + CO2 + HCHO + CCO-O2.
MPH2	Same k as rxn APH2				62,64	MA-RCO3. + HO2. = #.75 {RCO-OOH + O2} + #.25 {RCO-OH + O3} + XC
MPN3	Same k as rxn APN3				62,64	MA-RCO3. + NO3 = NO2 + CO2 + HCHO + CCO-O2. + O2
MPME	Same k as rxn APME				62,64	MA-RCO3. + C-O2. = RCO-OH + HCHO + XC + O2
MPRR	Same k as rxn APRR				62,64	MA-RCO3. + RO2-R. = RCO-OH + XC
MPR2	Same k as rxn APRR				43,62	MA-RCO3. + R2O2. = MA-RCO3.
MPRN	Same k as rxn APRR				62,64	MA-RCO3. + RO2-N. = #2 RCO-OH + O2 + #4 XC
MPAP	Same k as rxn APAP				62,64	MA-RCO3. + CCO-O2. = #2 CO2 + C-O2. + HCHO + CCO-O2. + O2
MPPP	Same k as rxn APAP				62,64	MA-RCO3. + RCO-O2. = HCHO + CCO-O2. + CCHO + RO2-R. + #2 CO2
MPBP	Same k as rxn APAP				62,64	MA-RCO3. + BZCO-O2. = HCHO + CCO-O2. + BZ-O. + R2O2. + #2 CO2
MPMP	Same k as rxn APAP				62,64	MA-RCO3. + MA-RCO3. = #2 {HCHO + CCO-O2. + CO2}
Other Organic Radical Species						
TBON	2.40e-11	2.40e-11			66,67	TBU-O. + NO2 = RNO3 + #-2 XC
TBOD	9.87e+2	7.50e+14	16.20		68,67	TBU-O. = ACET + C-O2.
BRN2	3.80e-11	2.30e-11	-0.30		69	BZ-O. + NO2 = NPHE
BRH2	Same k as rxn RRH2				70	BZ-O. + HO2. = PHEN
BRXX	1.00e-3	1.00e-3			71	BZ-O. = PHEN
BNN2	Same k as rxn BRN2				72	BZ(NO2)-O. + NO2 = #2 XN + #6 XC
BNH2	Same k as rxn RRH2				70	BZ(NO2)-O. + HO2. = NPHE
BNXX	Same k as rxn BRXX				71	BZ(NO2)-O. = NPHE
Explicit and Lumped Molecule Organic Products						
FAHV	Phot Set= HCHO_R				73	HCHO + HV = #2 HO2. + CO
FAVS	Phot Set= HCHO_M				73	HCHO + HV = H2 + CO



Table 46 (continued)

Label	Rate Parameters [a]				Refs & Notes	Reaction and Products [b]
	k(0)	A	Ea	B		
FAOH	9.20e-12	8.60e-12	-0.04		31	HCHO + HO. = HO2. + CO + H2O
FAH2	7.90e-14	9.70e-15	-1.24		31	HCHO + HO2. = HOCOO.
FAHR	1.51e+2	2.40e+12	13.91		31	HOCOO. = HO2. + HCHO
FAHN	Same k as rxn MER1				74	HOCOO. + NO = HCOOH + NO2 + HO2.
FAN3	5.74e-16	2.00e-12	4.83		75	HCHO + NO3 = HNO3 + HO2. + CO
AAOH	1.58e-11	5.60e-12	-0.62		31	CCHO + HO. = CCO-O2. + H2O
AAHV	Phot Set= CCHO_R				76	CCHO + HV = CO + HO2. + C-O2.
AAN3	2.73e-15	1.40e-12	3.70		77	CCHO + NO3 = HNO3 + CCO-O2.
PAOH	2.00e-11	2.00e-11			78,31,79,80	RCHO + HO. = #.034 RO2-R. + #.001 RO2-N. + #.965 RCO-O2. + #.034 CO + #.034 CCHO + #.003 XC
PAHV	Phot Set= C2CHO				78,76	RCHO + HV = CCHO + RO2-R. + CO + HO2.
PAN3	3.67e-15	1.40e-12	3.52		78,81	RCHO + NO3 = HNO3 + RCO-O2.
K3OH	1.92e-13	1.10e-12	1.03		31,82	ACET + HO. = HCHO + CCO-O2. + R2O2.
K3HV	Phot Set= ACETONE				83	ACET + HV = CCO-O2. + C-O2.
K4OH	1.18e-12	1.30e-12	0.05	2.0	31,79,80	MEK + HO. = #.37 RO2-R. + #.042 RO2-N. + #.616 R2O2. + #.492 CCO-O2. + #.096 RCO-O2. + #.115 HCHO + #.482 CCHO + #.37 RCHO + #.287 XC
K4HV	Phot Set= KETONE, qy= 1.5e-1				84	MEK + HV = CCO-O2. + CCHO + RO2-R.
MeOH	9.14e-13	3.10e-12	0.72	2.0	85	MEOH + HO. = HCHO + HO2.
MER9	5.49e-12	2.90e-12	-0.38		86	COOH + HO. = H2O + #.35 {HCHO + HO.} + #.65 C-O2.
MERA	Phot Set= COOH				87	COOH + HV = HCHO + HO2. + HO.
LPR9	1.10e-11	1.10e-11			88,89	ROOH + HO. = H2O + RCHO + #.34 RO2-R. + #.66 HO.
LPRA	Phot Set= COOH				90	ROOH + HV = RCHO + HO2. + HO.
GLHV	Phot Set= GLY_R				91,92	GLY + HV = #2 {CO + HO2.}
GLVM	Phot Set= GLY_ABS, qy= 6.0e-3				91,93	GLY + HV = HCHO + CO
GLOH	1.10e-11	1.10e-11			31,94,95	GLY + HO. = #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #.37 XC
GLN3	9.63e-16	2.80e-12	4.72		95,96	GLY + NO3 = HNO3 + #.63 HO2. + #1.26 CO + #.37 RCO-O2. + #.37 XC
MGHV	Phot Set= MGLY_ADJ				97	MGLY + HV = HO2. + CO + CCO-O2.
MGOH	1.50e-11	1.50e-11			31	MGLY + HO. = CO + CCO-O2.
MGN3	2.43e-15	1.40e-12	3.77		96	MGLY + NO3 = HNO3 + CO + CCO-O2.
BAHV	Phot Set= BACL_ADJ				91a,98	BACL + HV = #2 CCO-O2.
PHOH	2.63e-11	2.63e-11			99,100	PHEN + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 GLY + #4.1 XC
PHN3	3.78e-12	3.78e-12			99,101	PHEN + NO3 = HNO3 + BZ-O.
CROH	4.20e-11	4.20e-11			99,102	CRES + HO. = #.24 BZ-O. + #.76 RO2-R. + #.23 MGLY + #4.87 XC
CRN3	1.37e-11	1.37e-11			99,101	CRES + NO3 = HNO3 + BZ-O. + XC

Table 46 (continued)

Label	Rate Parameters [a]				Refs & Notes	Reaction and Products [b]
	k(0)	A	Ea	B		
NPN3	Same k as rxn PHN3				103	NPHE + NO3 = HNO3 + BZ(NO2)-O.
BZOH	1.29e-11	1.29e-11			99	BALD + HO. = BZCO-O2.
BZHV	Phot Set= BZCHO, qy= 5.0e-2				104	BALD + HV = #7 XC
BZNT	2.62e-15	1.40e-12	3.72		105	BALD + NO3 = HNO3 + BZCO-O2.
MAOH	3.36e-11	1.86e-11	-0.35		106,80,107	METHACRO + HO. = #.5 RO2-R. + #.416 CO + #.084 HCHO + #.416 MEK + #.084 MGLY + #.5 MA-RCO3. + #.0416 XC
MAO3	1.13e-18	1.36e-15	4.20		106,108, 109,110	METHACRO + O3 = #.008 HO2. + #.1 RO2-R. + #.208 HO. + #.1 RCO-O2. + #.45 CO + #.117 CO2 + #.2 HCHO + #.9 MGLY + #.333 HCOOH + #.0.1 XC
MAN3	4.58e-15	1.50e-12	3.43		106,111, 80,112	METHACRO + NO3 = #.5 {HNO3 + RO2-R. + CO + MA-RCO3.} + #1.5 XC + #.5 XN
MAOP	6.34e-12	6.34e-12			113,5	METHACRO + O3P = RCHO + XC
MAHV	Phot Set= ACROLEIN, qy= 4.1e-3				106,114	METHACRO + HV = #.34 HO2. + #.33 RO2-R. + #.33 HO. + #.67 CCO-O2. + #.67 CO + #.67 HCHO + #.33 MA-RCO3. + #.0 XC
MVOH	1.89e-11	4.14e-12	-0.90		106,80	MVK + HO. = #.3 RO2-R. + #.025 RO2-N. + #.675 R2O2. + #.675 CCO-O2. + #.3 HCHO + #.675 RCHO + #.3 MGLY + #.0.725 XC
MVO3	4.58e-18	7.51e-16	3.02		106,108, 109,80, 110	MVK + O3 = #.064 HO2. + #.05 RO2-R. + #.164 HO. + #.05 RCO-O2. + #.475 CO + #.124 CO2 + #.1 HCHO + #.95 MGLY + #.351 HCOOH + #.0.05 XC
MVN3	(Slow)				106	MVK + NO3 = #4 XC + XN
MVOP	4.32e-12	4.32e-12			113,5	MVK + O3P = #.45 RCHO + #.55 MEK + #.45 XC
MVHV	Phot Set= ACROLEIN, qy= 2.1e-3				106,114, 115	MVK + HV = #.3 C-O2. + #.7 CO + #.7 PROD2 + #.3 MA-RCO3. + #.2.4 XC
IPOH	6.19e-11	6.19e-11			116,106, 80	ISOPROD + HO. = #.705 RO2-R. + #.006 RO2-N. + #.0 R2O2. + #.289 MA-RCO3. + #.357 CO + #.056 HCHO + #.134 CCHO + #.015 RCHO + #.158 MEK + #.352 PROD2 + #.158 GLY + #.179 MGLY + #.0.514 XC
IPO3	4.18e-18	4.18e-18			116,106, 80,117, 109,118, 110	ISOPROD + O3 = #.4 HO2. + #.048 RO2-R. + #.048 RCO-O2. + #.285 HO. + #.498 CO + #.14 CO2 + #.125 HCHO + #.047 CCHO + #.21 MEK + #.023 GLY + #.742 MGLY + #.1 HCOOH + #.372 RCO-OH + #.33 XC
IPN3	1.00e-13	1.00e-13			116,106, 80	ISOPROD + NO3 = #.85 RO2-R. + #.15 MA-RCO3. + #.609 CO + #.15 HNO3 + #.241 HCHO + #.233 RCHO + #.008 MGLY + #.609 RNO3 + #.241 XN + #.827 XC
IPHV	Phot Set= ACROLEIN, qy= 4.1e-3				116,106, 80,119	ISOPROD + HV = #1.233 HO2. + #.467 CCO-O2. + #.3 RCO-O2. + #1.233 CO + #.3 HCHO + #.467 CCHO + #.233 MEK + #.233 XC

Table 46 (continued)

Label	Rate Parameters [a]				Refs & Notes	Reaction and Products [b]
	k(0)	A	Ea	B		
<u>Lumped Parameter Organic Products</u>						
K6OH	1.50e-11	1.50e-11			120	PROD2 + HO. = #.379 HO2. + #.473 RO2-R. + #.07 RO2-N. + #.029 CCO-O2. + #.049 RCO-O2. + #.213 HCHO + #.085 CCHO + #.559 RCHO + #.116 MEK + #.329 PROD2 + #.88 XC
K6HV	Phot Set= KETONE, qy= 2.0e-2				120,121	PROD2 + HV = #.915 RO2-R. + #.085 RO2-N. + #.677 R2O2. + #.4 CCO-O2. + #.6 RCO-O2. + #.304 HCHO + #.163 CCHO + #.782 RCHO + #.09 XC
RNOH	7.80e-12	7.80e-12			122	RNO3 + HO. = #.339 NO2 + #.113 HO2. + #.376 RO2-R. + #.172 RO2-N. + #.597 R2O2. + #.01 HCHO + #.44 CCHO + #.214 RCHO + #.006 ACET + #.177 MEK + #.048 PROD2 + #.31 RNO3 + #.351 XN + #.56 XC
RNHV	Phot Set= IC3ONO2				122,123	RNO3 + HV = NO2 + #.341 HO2. + #.565 RO2-R. + #.094 RO2-N. + #.152 R2O2. + #.134 HCHO + #.431 CCHO + #.147 RCHO + #.02 ACET + #.243 MEK + #.436 PROD2 + #.35 XC
<u>Uncharacterized Reactive Aromatic Ring Fragmentation Products</u>						
D1OH	5.00e-11	5.00e-11			124,125	DCB1 + HO. = RCHO + RO2-R. + CO
D1HV		(Slow)			124,126	DCB1 + HV = HO2. + #2 CO + RO2-R. + GLY + R2O2.
D1O3	2.00e-18	2.00e-18			124,127, 117	DCB1 + O3 = #1.5 HO2. + #.5 HO. + #1.5 CO + #.5 CO2 + GLY
D2OH	5.00e-11	5.00e-11			128,129	DCB2 + HO. = R2O2. + RCHO + CCO-O2.
D2HV	Phot Set= MGLY_ABS, qy= 3.7e-1				128,130	DCB2 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}
D3OH	5.00e-11	5.00e-11			128,129	DCB3 + HO. = R2O2. + RCHO + CCO-O2.
D3HV	Phot Set= ACROLEIN, qy= 7.3e+0				128,130	DCB3 + HV = RO2-R. + #.5 {CCO-O2. + HO2.} + CO + R2O2. + #.5 {GLY + MGLY + XC}
<u>Explicit Primary Organics</u>						
c1OH	6.37e-15	2.15e-12	3.45		31	CH4 + HO. = H2O + C-O2.

[a] Except as indicated, the rate constants are given by  $k(T) = A \cdot (T/300)^B \cdot e^{-E_a/RT}$ , where the units of k and A are  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ ,  $E_a$  are  $\text{kcal mol}^{-1}$ , T is  $^{\circ}\text{K}$ , and  $R=0.0019872 \text{ kcal mol}^{-1} \text{deg}^{-1}$ . The following special rate constant expressions are used:

Phot Set = name: The absorption cross sections and quantum yields for the photolysis reaction are given in Table 46, where “name” indicates the photolysis set used. If a “qy=number” notation is given, the number given is the overall quantum yield, which is assumed to be wavelength independent.

Falloff: The rate constant as a function of temperature and pressure is calculated using

$k(T,M) = \{k_0(T) \cdot [M] / [1 + k_0(T) \cdot [M] / k_{\text{inf}}(T)]\} \cdot F^Z$ , where  $Z = \{1 + [\log_{10}\{k_0(T) \cdot [M] / k_{\text{inf}}(T)\}]^2\}^{-1}$ , [M] is the total pressure in molecules  $\text{cm}^{-3}$ , F is as indicated on the table, and the temperature dependences of  $k_0$  and  $k_{\text{inf}}$  are as indicated on the table.

Table 46 (continued)

- 
- (Slow): The reaction is assumed to be negligible and is not included in the mechanism. It is shown on the listing for documentation purposes only.
- $k = k_0 + k_3 M(1 + k_3 M/k_2)$ : The rate constant as a function of temperature and pressure is calculated using  $k(T, M) = k_0(T) + k_3(T) \cdot [M] \cdot (1 + k_3(T) \cdot [M]/k_2(T))$ , where  $[M]$  is the total bath gas (air) concentration in molecules  $\text{cm}^{-3}$ , and the temperature dependences for  $k_0$ ,  $k_2$  and  $k_3$  are as indicated on the table.
- $k = k_1 + k_2 [M]$ : The rate constant as a function of temperature and pressure is calculated using  $k(T, M) = k_1(T) + k_2(T) \cdot [M]$ , where  $[M]$  is the total bath gas (air) concentration in molecules  $\text{cm}^{-3}$ , and the temperature dependences for  $k_1$ , and  $k_2$  are as indicated on the table.
- Same  $k$  as Rxn *label*: The rate constant is the same as the reaction with the indicated label.
- [b] Format of reaction listing: “=” separates reactants from products; “#*number*” indicates stoichiometric coefficient, “#*coefficient* { *product list* }” means that the stoichiometric coefficient is applied to all the products listed.

Table 47. Documentation notes for the base mechanism.

No.	Note
1	See Table 48 for listing of absorption cross sections and quantum yields. Set used is given in the "Type" column.
2	Absorption cross sections and quantum yields from IUPAC recommendation (Atkinson et al, 1997a), except that quantum yields for $\lambda > 410$ nm are from NASA (1997), which are consistent with IUPAC (Atkinson et al, 1997a) values except they are more precise. Note that more recent IUPAC recommendations (Atkinson et al, 1997b) gives slightly different absorption cross sections based on data from a more recent study, but the differences are not significant.
3	Rate constant expression derived from IUPAC (Atkinson et al, 1997b) recommendations for M = 20.9% O <sub>2</sub> and 79.1% N <sub>2</sub> .
4	Rate constant is IUPAC, Supplement VI (Atkinson et al, 1997b) and NASA (1997) recommendation.
5	This reaction is probably not important in the troposphere, but is included to increase range of applicability.
6	Rate constant expression is IUPAC (Atkinson et al, 1997b) recommendation.
7	Recommended rate constant given for N <sub>2</sub> is assumed to be applicable to air.
7a	The falloff parameters recommended by NASA (1997) give a 300K, 1 atm rate constant which is approximately 13% lower than the IUPAC-recommended values that were used.
8	The data of Mentel et al (1996) indicate that the reaction occurs through pathways which are first order and second order in H <sub>2</sub> O, where the latter is presumed to be surface-dependent. We assume that the process which is first order in H <sub>2</sub> O represents a gas-phase reaction, and use the rate expression of Mentel et al (1996) for this process. Note that the IUPAC (Atkinson et al, 1997b) recommendation that the gas-phase rate constant is less than $2 \times 10^{-21}$ cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> .
9	Photolysis of N <sub>2</sub> O <sub>5</sub> is assumed to be negligible compared to decomposition under atmospheric conditions.
10	The NASA (1997) evaluation states that the existence of this channel has not been firmly established, but results of a number of studies indicate it may occur. Rate constant expression used is that NASA (1997) states gives best fits to the data. Uncertainty is at least a factor of 2. This reaction was not discussed in the recent IUPAC evaluations (Atkinson et al, 1997a,b).
11	Absorption cross sections from IUPAC (Atkinson et al, 1997a). Values recommended by more recent IUPAC evaluation (Atkinson et al, 1997b) appear to be the same for 298K, though different at lower temperature. Temperature dependence ignored.
12	IUPAC (1997b) and NASA (1997) give no useable recommendations for quantum yields except to recommend that $q_y(\text{NO}_2+\text{O})=1$ for $\lambda \leq 583$ . Quantum yields of Magnotta and Johnson (1980), scaled down by a factor of 1.5 to give unit maximum quantum yields, as incorporated in mechanism of Carter (1990) were retained in this mechanism. The calculated rate constant for solar overhead sun is consistent with the recommendations of Magnotta and Johnson (1980), and reasonably consistent with the IUPAC (1997a) recommendation.

Table 47 (continued)

No.	Note
13	Absorption cross sections from IUPAC, given for T=273K (Atkinson et al, 1997b). Temperature dependences for cross section (NASA, 1997) are ignored.
14	Quantum yields for O1D are those tabulated by IUPAC (Atkinson et al, 1997b), which are significantly higher than previous recommendations at $\lambda > 310$ nm. Quantum yields for O3P based on assuming total quantum yield of unity, though this was not adequately discussed in the evaluations.
15	Calculated using IUPAC (Atkinson et al, 1997b) recommended rate constants for reaction with O2 and N2, assuming 20.9% O2 and 79.1% N2. Temperature dependence optimized to fit rate constants calculated for T= 270, 300, and 330K.
16	Falloff expression recommended by NASA (1997) used because it gives rate constant for 1 atm N2 which is consistent with measurement near those conditions. IUPAC (Atkinson et al, 1997a,b) recommendations are not used because k (1 atm N2) are not consistent with these data, being based on high pressure data in He. This is consistent with current recommendation of Atkinson (private communication, 1997).
17	The cross sections from Stockwell and Calvert (1978), used in the previous version of the mechanism, are retained because they are higher resolution than the averaged data recommended by IUPAC (1997b), and the areas under the spectra appear to be consistent.
18	Quantum yields are those recommended by IUPAC (Atkinson et al, 1997b).
19	NASA (1997) and IUPAC (Atkinson et al, 1997a,b) give significantly different recommendations for rate parameters for this important reaction. The falloff expression used here is based on a NASA (1997) and IUPAC (Atkinson et al, 1997a,b) give significantly different recommendations for rate parameters for this important reaction. The falloff expression used here is based on a re-evaluation of the data by Golden (Personal communication, 1998), and is expected to be the recommendation in the next NASA evaluation. This is essentially the same as the NASA (1997) recommendation except for the temperature dependence, which Golden says was due to improper uncertainty weighting. The data with "weak colliders (i.e., bath gases other than SF6 or CF4) appear to be well fit by this parameterization, including the data of Donahue et al (1997). The data of Forster et al (1995), which are the basis for the high 1997 IUPAC recommendation, are not used because they may be due to a HOONO-forming channel becoming importa
20	No recommendation is given concerning the temperature dependence of this rate constant, which is assumed to be small.
21	The rate parameters were derived to fit the rate constants calculated using the NASA (1997) recommended expression for T 270 - 330 K range and 1 atm. total pressure.
22	This rate constant is strictly valid for 1 atm air only, but the error introduced by neglecting the pressure dependence of this reaction is expected to be small.
23	Absorption cross-sections from IUPAC (Atkinson et al, 1997b). Recommend quantum yield for the OH + NO2 pathway is "close to unity" for $\lambda > 260$ nm, though other pathways become important at lower wavelengths.
24	The rate constants for the OH + CO reactions are based on expression given by IUPAC (Atkinson et al, 1997a). NASA (1997) gives a similar expression, but without temperature dependence.

Table 47 (continued)

No.	Note
25	Absorption cross sections and quantum yields from IUPAC (Atkinson et al, 1997b). Quantum yields are uncertain and based on data for a single wavelength only.
26	Reactions and rate constants used for the HO <sub>2</sub> + HO <sub>2</sub> and HO <sub>2</sub> + HO <sub>2</sub> + H <sub>2</sub> O system based on the data of Kircher and Sander (1984) as discussed in the IUPAC (Atkinson et al, 1997b) evaluation.
27	Rate constant recommended by IUPAC (Atkinson et al, 1997b). Measurement of the branching ratios vary, so the mechanism is uncertain. The branching ratio assumed is approximately in the middle of the range given by IUPAC (Atkinson et al, 1997b) and NASA (1997) evaluations, which is 0.6 - 1.0 for the OH-forming channel.
28	Rate expression from NASA (1994) evaluation. More recent evaluations neglect this reaction, though it may be non-negligible under some nighttime conditions (Stockwell et al, 1997).
29	Absorption cross sections recommended by IUPAC (Atkinson et al, 1997a,b) used. Quantum yield assumed to be unity.
30	The initially formed HOSO <sub>2</sub> is believed to react primarily with O <sub>2</sub> , forming HO <sub>2</sub> and SO <sub>3</sub> (Stockwell and Calvert, 1983). The SO <sub>3</sub> is assumed to be converted into sulfates, which are represented by the SULF model species.
31	Rate constant expression recommended by IUPAC, Supplement VII (Atkinson et al, 1999).
32	The reaction of NO <sub>2</sub> is ignored because it is rapidly reversed by the decomposition of the peroxyxynitrate, resulting in no net reaction. Calculations not neglecting peroxyxynitrate formation give essentially the same results. However, this may not be valid in low temperature simulations.
33	Total rate constant and rate constant for methoxy radical formation from IUPAC (Atkinson et al, 1997a, 1999) recommendation. Temperature dependence for rate constant for methanol + HCHO formation derived to be consistent with these.
34	The RO <sub>2</sub> -R. operator represents the effects of peroxy radicals which react with NO to form NO <sub>2</sub> and HO <sub>2</sub> , and also the effects of peroxy radical reactions on other species. Except as indicated, the organic products from this peroxy radical are not represented.
35	Rate constant recommended by Atkinson (1997a) for general peroxy radicals.
36	The organic products from the HO <sub>2</sub> reaction are represented by the lumped higher hydroperoxide species. Negative "lost carbons" are added because this is a zero-carbon operator.
37	Rate constant based on that recommended by IUPAC (Atkinson et al, 1999) for ethyl peroxy + NO <sub>3</sub> . Formation of alkoxy + NO <sub>2</sub> + O <sub>2</sub> stated to occur >85% of the time.
38	The reaction is assumed to form the corresponding alkoxy radical. The HO <sub>2</sub> represents the radicals regenerated by the alkoxy radical.
39	Based on rate constant for methyl peroxy + ethyl peroxy rate given by Atkinson (1997a). This is near the middle of the range of rate constants given for other methyl peroxy + higher alkyl peroxy radical reactions given by Atkinson (1997a) or Atkinson et al (1997a).
40	Approximately half of the peroxy + peroxy reaction is assumed to form two O <sub>2</sub> + alkoxy radicals, where the latter react to form HO <sub>2</sub> and organic products, where the formaldehyde from the

Table 47 (continued)

No.	Note
	methoxy is represented in this reaction. The HO2 represents the radicals regenerated in the fraction of this peroxy radical which reacts in this way. The other half of the time the reaction is assumed to proceed via H-atom transfer, with half of that involving transfer from the methyl peroxy, forming formaldehyde, and the other half involving transfer to the methyl peroxy, forming methanol. Note that the organic products from RO2-R· are not represented in this reaction because this is a “massless” operator.
41	The rate constants for peroxy + peroxy radical reactions can vary by orders of magnitude depending on the type of radical (e.g., Atkinson, 1997), so the value used here must be approximate. The value used is the geometric mean of the values recommended by Atkinson (1997a) for primary + primary and secondary + secondary peroxy radicals.
42	Assumed to have same rate constant as used for general higher peroxy radical (see notes for RO2-R.).
43	The R2O2. operator represents the effects of peroxy radical reactions causing extra NO to NO2 conversions. Its reactions with species other than NO are represented as having no effect other than to consume this operator.
44	The RO2-N. operator represents the effects of peroxy radicals which react with NO to form higher organic nitrates (represented by RNO3), and also the effects of peroxy radical reactions on other species. It has five carbons.
45	The organic products from the HO2 reaction are represented by the lumped higher hydroperoxide species. "Lost carbons" are added because this is a five-carbon operator.
46	Approximately half of the peroxy + peroxy reaction for radicals represented by RO2-N. is assumed to form two O2 + alkoxy radicals. The MEK + HO2. represents the products and radicals formed from the alkoxy radical from this species. The other half is assumed to involve disproportionation, forming O2 + and an alcohol and carbonyl compound. These are represented by PROD2.
47	This reaction is assumed to form the corresponding alkoxy radical, which is assumed to react products represented by MEK + HO2.
48	Falloff expression recommended by IUPAC (Atkinson et al, 1997a, 1999), based on data of Bridier et al (1991).
49	Falloff expression recommended by IUPAC (Atkinson et al, 1992), based on data of Bridier et al (1991). Note: NASA (1997) also recommends using Bridier et al (1991) data, but gives a revised expression which gives a different k at 298K. Based on new data on PAN decomposition which give a factor of ~2 lower rate 298K rate constants, IUPAC (1997a, 1999) recommends the a high pressure rate constant expression of $5.4 \times 10^{16} \exp(-13830/T)$ , derived by averaging the data. We are staying with the earlier IUPAC Recommendations based on the data of Bridier et al (1991) because it gives good agreement with the data of Tuazon et al (1991a) and is consistent with the NASA (1997) recommended equilibrium constant.
50	Rate constant expression recommended by IUPAC (Atkinson et al, 1999). This is almost the same as the earlier IUPAC(Atkinson et al, 1997a) recommended value of $2.0 \times 10^{-11}$ and close to the NASA (1997) value of $1.8 \times 10^{-11}$ .



Table 47 (continued)

No.	Note
51	Branching ratio and rate constant expression recommended by IUPAC (Atkinson et al, 1997a, 1999).
52	Rate constant from Canosa-Mass et al (1996)
53	Rate constant expression recommended by IUPAC (Atkinson et al, 1999) evaluation. As discussed there, the data are inconclusive as to the importance of the competing reaction forming $\text{CH}_3\text{O} + \text{CH}_3\text{CO}_2 + \text{O}_2$ , but the study which indicate that it occurs, which was used in the previous IUPAC (Atkinson et al, 1997a) evaluation, indicates that it occurs less than ~15% under atmospheric conditions. Therefore, the reaction is assumed to involve disproportionation 100% of the time.
54	Rate constant is the average of the the IUPAC (Atkinson et al, 1999) recommendations of $1 \times 10^{-11}$ for the acetyl peroxy + ethyl peroxy reaction and $5 \times 10^{-12}$ for the acetyl peroxy + $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ reaction.
55	This reaction is assumed to proceed primarily by disproportionation to form the organic acid and a carbonyl compound, based on data for the acetyl peroxy + methyl peroxy reaction.
56	The rate parameters are assumed to be approximately the same as those for the reaction of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ at the high pressure limit. This assumption is employed in the IUPAC (Atkinson et al, 1999) evaluation when deriving the recommended value of the $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OO}\cdot + \text{NO}_2$ rate constant.
57	The products of the reactions of $\text{RCO-O}_2\cdot$ are based on $\text{R}=\text{ethyl}$ . Mechanism assumed to be similar to corresponding reaction of acetyl peroxy radicals.
58	Rate parameters based on the IUPAC (Atkinson et al, 1999) recommendation for PPN.
58a	Rate constant expression based on the data of Seefeld and Kerr (1997), which gives $k(\text{PPN2})/k(\text{PPNO}) = 2.33 \pm 0.38$ , and the value of $k(\text{PPN2})$ used in the mechanism. This is as recommended by IUPAC (Atkinson et al, 1999).
59	Assumed to have same rate constant as corresponding reaction of $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ .
60	Rate constant based on $k(\text{NO}_2)/k(\text{NO})$ ratio measured by Kirchner et al (1992) and the $k(\text{NO})$ used for general higher acyl peroxy radical species.
61	Rate constant expression based on the data of Kirchner et al (1992).
62	Assumed to have the same rate constant and mechanism as used for the general higher acyl peroxy radical or higher PAN analogue
63	The mechanism is assumed to be analogous to the mechanism of the corresponding reaction of acetyl peroxy radicals. Note that the formation of benzyl peroxy radicals results in the formation of phenoxy after 1 NO to $\text{NO}_2$ conversion, so it can be represented by $\text{BZ-O}\cdot + \text{R}_2\text{O}_2$ . The general lumped higher organic acid ( $\text{RCO-OH}$ ) and peroxyacid ( $\text{RCO-OOH}$ ) are used to represent the aromatic acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.
64	MA- $\text{RCO}_3$ . And MA-PAN are used to represent the acyl peroxy radical and PAN analogue formed from any acrolein compound. Their reactions are based on those formed from methacrolein. Generally, the reaction mechanisms are assumed to be analogous to those for the

Table 47 (continued)

No.	Note
	corresponding reactions of acetyl peroxy radicals. The alkoxy radical is assumed to decompose to $\text{CO}_2 + \text{CH}_2=\text{CH}(\cdot)\text{CH}_3$ , while the latter reacts with $\text{O}_2$ to form $\text{HCHO} + \text{CH}_3\text{CO}\cdot$ , as discussed by Carter and Atkinson (1996). The general lumped higher organic acid ( $\text{RCO-OH}$ ) and peroxyacid ( $\text{RCO-OOH}$ ) are used to represent the unsaturated acids and peroxyacids expected to be formed in the peroxy + peroxy reactions.
65	Rate parameters from Roberts and Bertman (1992), as used by Carter and Atkinson (1996).
66	The rate expression recommended by Atkinson (1997) for general alkoxy + $\text{NO}_2$ reactions is $2.3 \times 10^{-11} \exp(+150/T)$ . This is reduced by a factor of 1.58 to be consistent with environmental chamber data, as discussed in a separate note.
67	The effects of isobutane on ozone formation and radical levels in environmental chamber experiments are not consistent with predictions of models which assume the recommended rate constant ratios for the decomposition of t-butoxy radicals relative to reaction with $\text{NO}_2$ . The data are better fit if the ratio is increased by a factor of 2.5. The error is assumed to be equally distributed in each rate constant, so they are both adjusted by the a factor of 1.58, which is the square root of 2.5. This rate constant must be considered to be uncertain by at least this amount.
68	Atkinson (1997b) recommends the high-pressure rate expression of $6.0 \times 10^{-14} \exp(-16.2/RT)$ . Batt and Robinson (1987) calculate that at one atmosphere the rate constant is 79% the high pressure limit, giving an estimated rate expression of $4.74 \times 10^{-14} \exp(-16.2/RT)$ . This is increased by a factor of 1.58 to be consistent with environmental chamber data, as discussed in a separate note. This rate constant must be considered to be uncertain by at least this amount.
69	The rate constant is based on the general recommendation of Atkinson (1994) for alkoxy + $\text{NO}_2$ reactions at the high pressure limit. Nitrophenol formation has generally been assumed in this reaction (e.g., see Atkinson, 1990; Carter, 1990), presumably via some rearrangement of an initially-formed unstable adduct. However, based on lower than expected yields of nitrophenols in $\text{NO}_3$ + cresol and $\text{OH}$ + benzaldehyde systems (Atkinson, 1994), this may be an oversimplification.
70	Assumed to have the same rate constant as the reaction of $\text{HO}_2$ with peroxy radicals. This may underestimate the actual rate constant because alkoxy radicals tend to be more reactive than peroxy radicals.
71	This is included to avoid problems if these radicals are ever formed under conditions where both $\text{HO}_2$ and $\text{NO}_2$ are very low (which is considered to be unlikely under most ambient conditions), and can be considered to represent its reaction with organics present. The rate constant is arbitrary, and is such that this process becomes significant only if $[\text{NO}_2] < \sim 3 \times 10^{-6}$ ppm and $[\text{HO}_2] < 1 \times 10^{-5}$ ppm.
72	The rate constant is based on the general recommendation of Atkinson (1994) for alkoxy + $\text{NO}_2$ reactions at the high pressure limit. The products of this reaction (presumed to be aromatic dinitro compounds) are expected to have very low vapor pressures and are represented as unreactive nitrogen and carbon.
73	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a) used. Absorption cross sections used are those given for $T = 285\text{K}$ .

Table 47 (continued)

No.	Note
74	Rate constant assumed to be the same as used for methylperoxy + NO.
75	T=298K Rate constant recommended by IUPAC (Atkinson et al, 1979a). Temperature dependence is as estimated by IUPAC (Atkinson et al, 1979a).
76	Absorption cross sections and quantum yields recommended by IUPAC (Atkinson et al, 1997a, 1999) used. Reaction assumed to occur primarily by breaking the C-CHO bond. Pathway forming molecular products is assumed to be negligible under atmospheric conditions, based on calculated rate for analogous reaction of acetaldehyde.
77	Rate constant expression recommended by IUPAC, Supplement V (Atkinson et al, 1997a).
78	The mechanism for RCHO is based on reactions estimated for propionaldehyde.
79	OH reactions at various positions in the molecule estimated using the group-additivity methods of Kwok and Atkinson (1995), as updated by Kwok et al (1996).
80	Except as indicated by other footnotes, the overall reaction mechanism was derived using the general estimation methods for atmospheric reactions of alkyl, alkyl peroxy, and alkoxy radicals and the automated mechanism generation system as discussed by Carter (1999).
81	The rate constant is based on the estimated rate constant for the reaction of NO <sub>3</sub> with propionaldehyde. This is based on the correlation noted by Atkinson (1991) between HO and NO <sub>3</sub> radical H-atom abstraction rate constants, the assumption that the reaction only occurs at the -CHO group, and the estimated rate constant for OH reaction at that group. Atkinson (1991) noted that 298K H abstraction rate constants per abstractable hydrogen are approximately fit by $\ln k_{\text{NO}_3} \approx 6.498 + 1.611 \ln k_{\text{OH}}$ , and the rate constant for OH abstraction from the -CHO group estimated by group additivity methods is $k_{\text{OH}} = 1.94 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . These correspond to $k_{\text{NO}_3} \approx 3.67 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298K. The temperature dependence is derived by assuming the same A factor as that for the reaction of NO <sub>3</sub> with acetaldehyde.
82	Reaction in the presence of NO <sub>x</sub> is assumed to involve formation of CH <sub>3</sub> C(O)CH <sub>2</sub> O., after one NO to NO <sub>2</sub> conversion. Based on the data of Jenkin et al (1993), this radical is believed to rapidly decompose to HCHO + CH <sub>3</sub> CO.
83	Absorption cross sections and quantum yields used are those recommended by IUPAC (Atkinson et al, 1997a) except as noted. The reported quantum yields at 230 and 330 are expected to be high and an estimated correction was made as discussed by Carter et al (1993b). The corrected quantum yield data for wavelengths less than 290 nm were then fit to a smooth curve to estimate the quantum yields for higher wavelengths, with no weight being given to the highly uncertain 330 nm point. As discussed by Carter et al (1993b), using these corrections results in better fits of model calculations to environmental chamber experiments involving acetone.
84	The absorption coefficients used for MEK are from Moortgat (Private communication, 1996). The overall MEK quantum yield of 0.15 was found to give best fits to the MEK-NO <sub>x</sub> and MEK reactivity data our laboratories (Carter et al, 1999a). This is slightly higher than the overall quantum yield of 0.1 used in the previous version of the mechanism, based on fits to UNC outdoor chamber data (Carter, 1990). Using an overall quantum yield was found to give better fits to the data using both xenon arc and blacklight light sources than assuming wavelength-

Table 47 (continued)

No.	Note
	dependence quantum yields such as for acetone. The reaction is assumed to proceed primarily by breaking the weakest CO-C bond.
85	The mechanism and rate constants are as recommended by IUPAC (Atkinson et al, 1997a, 1999). 85% of the reaction is believed to involve formation of $\cdot\text{CH}_2\text{OH}$ , with the remainder involving formation of $\text{CH}_3\text{O}\cdot$ . However, both these radicals react primarily with $\text{O}_2$ forming formaldehyde + $\text{HO}_2$ , so the overall process is as shown.
86	Rate constant and branching ratio for initial OH reaction based on IUPAC (Atkinson et al, 1997a, 1999) recommendation. The $\cdot\text{CH}_2\text{OOH}$ radical is assumed to rapidly decompose to $\text{HCHO} + \text{OH}$ , based on its high estimated exothermicity.
87	Absorption cross sections from IUPAC (Atkinson et al, 1997a, 1999), which also recommends assuming unit total quantum yield, but gives no recommendation as to the exact mechanism. Breaking the O-O bond assumed to be the major pathway.
88	The mechanism for ROOH is based on reactions estimated for n-propyl hydroperoxide.
89	Reaction at the OOH position is assumed to be as fast as in $\text{CH}_3\text{OOH}$ . Reaction at the 1-position is estimated to be $\sim 7 \times 10^{-12}$ (i.e., $\sim 2/3$ of the time) based on comparing rates of analogous reactions for methanol, ethanol, and $\text{CH}_3\text{OOH}$ (IUPAC, 1997a, 1999). The alpha-hydroperoxy radicals are assumed to decompose rapidly to OH and the carbonyl on the basis of estimated high exothermicity. Reaction at the 2- or 3-positions are estimated to occur no more than $\sim 10\%$ of the time and are neglected.
90	Reaction assumed to occur with the same rate and analogous mechanism as methyl hydroperoxide.
91	Absorption cross sections from Plum et al (1983), as recommended by IUPAC (Atkinson et al, 1997a, 1999).
91a.	Absorption cross sections from Plum et al (1983). The evaluations give no recommendations for biacetyl.
92	For the low wavelength band, a constant quantum yield of 0.4 is assumed, based on data of Langford and Moore (1984). For the high wavelength band, quantum yield is assumed to decrease linearly to zero at the threshold wavelength of 418 nm, starting at a "falloff" wavelength, which is adjusted to yield fits to chamber data for acetylene - $\text{NO}_x$ and acetylene reactivity experiments, as discussed by Carter et al (1997c). "Best fit" falloff wavelength of 380 nm used. Note that this gives overall quantum yields which are $\sim 1.4$ times higher than overall quantum yield reported by Plum et al (1983) for conditions of those experiments. Although use of acetylene reactivity data is a highly indirect way to obtain glyoxal quantum yields, it is considered to be a less uncertain way to estimate radical quantum yields than the data of Plum et al (1993), which uses a UV-poor light source and only measures rates of glyoxal decay.
93	Plum et al (1983) observed 13% formaldehyde yield in photodecomposition, so overall quantum yield adjusted to give this yield relative to the radical forming process for the spectral distribution of those experiments. A wavelength-independent quantum yield is used because of lack of information on wavelength dependence.

Table 47 (continued)

No.	Note
94	Product distribution based on the data of Niki et al (1985), as discussed by IUPAC (Atkinson et al, 1997a). Product distribution is calculated for 1 atm air at 298K.
95	HCO(CO)OO. is represented by the lumped higher acyl peroxy species RCO-OO.
96	The rate constant is estimated based on the correlation noted by Atkinson (1991) between HO and NO <sub>3</sub> radical H-atom abstraction rate constants, where the 298K H abstraction rate constants per abstractable hydrogen are approximately fit by $\ln k_{\text{NO}_3} = 6.498 + 1.611 \ln k_{\text{OH}}$ . The 298K rate constant is then derived from the 298K OH radical rate constant, assuming that all the reaction is at the OH group, and the temperature dependence is derived by assuming the same A factor per abstractable hydrogen as that for the reaction of NO <sub>3</sub> with acetaldehyde.
97	Absorption cross sections obtained from Moortgat (personal communication, 1996). These are essentially the same as those recommended by IUPAC (Atkinson et al, 1997a, 1999), except slightly better resolution. Photolysis at the low wavelength band is assumed to have unit quantum yields, based on data for biacetyl. Photolysis above the cutoff wavelength of 421 nm (Atkinson et al, 1977a) is assumed to have zero quantum yields. For the rest of the high wavelength region, the wavelength dependence was derived by assuming the quantum yields decline linearly from 1 at 344 nm to 0 at a wavelength (407 nm) which was adjusted to be such that the calculated overall quantum yields for the conditions of the experiments of Plum et al (1983) agreed with the overall quantum yield they observed experimentally. The quantum yields recommended by IUPAC (Atkinson et al, 1999) lack sufficient wavelength resolution to be useful for modeling.
98	Assumed to have unit quantum yield at low wavelength band based on data cited by Atkinson (1994). For the high wavelength band, the quantum yields were assumed to decline linearly from 1 at 350 nm to 0 at a wavelength (420 nm) which was adjusted to be such that the calculated overall quantum yields for the conditions of the experiments of Plum et al (1983) agreed with the overall quantum yield they observed experimentally.
99	Rate constant recommended by Atkinson (1994) for o-cresol.
100	The parameterized mechanism is estimated by analogy to the parameterized mechanism derived for cresols (see footnotes for OH + cresol reaction).
101	In absence of definitive data concerning this reaction, the same mechanism is used as assumed by Carter (1990). However, see footnotes concerning phenoxy reactions.
102	The parameterized mechanism is based on that used by Carter (1990), but was reoptimized to fit the NO, ozone, PAN, and cresol data in the o-cresol - NO <sub>x</sub> experiment EC281.
103	Assumed to have the same rate constant as the reaction of NO <sub>3</sub> with phenol. Reaction with NO <sub>3</sub> is assumed to dominate over reaction with OH radicals and other loss processes.
104	Absorption coefficients are from Majer et al (1969). The overall quantum yield derived by Carter (1990), which are based on model simulations of benzaldehyde decay rates in SAPRC evacuable chamber experiments, is used. Because of lack of data, the quantum yield is assumed to be independent of wavelength. The products formed from benzaldehyde photolysis are unknown, except that both radical formation and benzene formation appear to be minor (Carter, 1990). This benzaldehyde photolysis mechanism gives reasonably good model simulations of benzaldehyde -

Table 47 (continued)

No.	Note
	NO <sub>x</sub> experiments recently carried out in the CE-CERT xenon Teflon chamber (Carter et al, 1998a).
105	T=298K rate constant recommended by Atkinson (1994). Temperature dependence estimated by assuming the reaction has the same A factor as the reaction of NO <sub>3</sub> with acetaldehyde.
106	The rate constant and mechanism of Carter and Atkinson (1996) was used with no significant changes (except as indicated in other footnotes, if applicable). Some minor changes in product yields may result in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction scheme.
107	MEK is used to represent hydroxyacetone.
108	The excited HCHO <sub>2</sub> biradical is assumed to react as recommended by Atkinson (1997) based on data for the O <sub>3</sub> + ethene system, i.e., 37% stabilization, 12% decomposition to HCO + OH, 13% decomposition to CO <sub>2</sub> + H <sub>2</sub> , and 38% decomposition to CO + H <sub>2</sub> O. Note that this is different than used for this species when formed in the isoprene products mechanisms of Carter and Atkinson (1996) and Carter (1996).
109	The vibrationally excited HCOC(CH <sub>3</sub> )CO <sub>2</sub> biradicals are assumed to rearrange and decompose to HCOC(O)CH <sub>2</sub> + OH, where the former forms HCOC(O) + HCHO after O <sub>2</sub> addition and NO to NO <sub>2</sub> conversion. RCO-O <sub>2</sub> is used to represent HCOC(O)OO. in this reaction. Vibrationally excited CH <sub>3</sub> C(O)CHO <sub>2</sub> is assumed to rapidly convert to HCOC(CH <sub>3</sub> )CO <sub>2</sub> as discussed by Carter and Atkinson (1996).
110	The organic acid(s) formed in this reaction represent the formation of stabilized Crigee biradicals, which are assumed to be consumed primarily by reaction with H <sub>2</sub> O forming the corresponding acid.
111	NO <sub>3</sub> radical addition assumed to occur primarily at the least substituted position.
112	The product CH <sub>3</sub> C(O)CH <sub>2</sub> ONO <sub>2</sub> is expected to be relatively unreactive and is represented as "lost nitrogen" + 3 "lost carbons".
113	Rate constant estimated from linear correlation between log k for OH and O <sub>3</sub> P reaction. Chamber data for C <sub>3+</sub> alkenes are better fit by models assuming O <sub>3</sub> P reactions with C <sub>3+</sub> species do not form radicals. Stable products represented by the lumped higher aldehyde or ketone, depending on type of product(s) expected to be formed.
114	The overall quantum yield was reoptimized to fit the same data as discussed by Carter and Atkinson (1996). In the case of methacrolein, he changes to the other portion of the mechanism resulted in an ~14% increase in the best fit overall quantum yield compared to that derived by Carter and Atkinson (1996). In the case of MVK, the best fit overall quantum yield decreased by a factor of 5.
115	CH <sub>2</sub> =CHC(O)OO. Is represented by MA-RCO <sub>3</sub> .
116	As discussed by Carter (1996), ISOPROD is the "four product" lumped isoprene product species whose mechanism is derived by lumping rate constant and product parameters for a mixture of 30% hydroxymethacrolein, and 70% equal amounts of cis and trans HCOC(CH <sub>3</sub> )=CHCH <sub>2</sub> OH and HCOCH=C(CH <sub>3</sub> )CH <sub>2</sub> OH. These proportions are based on the estimated yields of these products

Table 47 (continued)

No.	Note
	in the reactions of OH with isoprene (Carter and Atkinson, 1996), which are represented by ISOPROD in the four product condensed mechanism (Carter, 1996). The other footnotes refer to the estimated mechanisms for these four individual compounds which were used to derive the lumped ISOPROD mechanism. RCHO, PROD2, MA-RCO3, etc. are used to represent various compounds as indicated in the descriptions of these lumped model species. See Carter and Atkinson (1996) for the specific compounds which can be formed in the various reactions of these species.
117	The HC(O)CHO <sub>2</sub> biradical can decompose either to OH + HCO + CO via an internal H abstraction from HCO, or to HCO + HCO <sub>2</sub> via rearrangement to HCOCH(O.)O. and decomposition. (The HCO would form HO <sub>2</sub> + CO and the HCO <sub>2</sub> would form HO <sub>2</sub> + CO <sub>2</sub> after reaction with O <sub>2</sub> .) These two pathways are assumed to have equal probability. Note that decomposition for these biradicals is assumed to be faster than for biradicals such as CH <sub>3</sub> CHO <sub>2</sub> because of the weaker H-CO and C-CO bonds.
118	The excited CH <sub>3</sub> C(O <sub>2</sub> )CH <sub>2</sub> OH biradical is assumed to react primarily via rearrangement to the unsaturated hydroperoxide followed by decomposition to OH radicals and the corresponding carbonyl compound, as is assumed in the general alkene mechanism (Carter, 1999b). Two possible such rearrangements can occur in the case of this biradical, one to CH <sub>2</sub> =C(OOH)CH <sub>2</sub> OH, which decomposes to OH + HOCH <sub>2</sub> C(O)CH <sub>2</sub> ., and the other to HOCH=C(OOH)CH <sub>3</sub> , which decomposes to OH + CH <sub>3</sub> C(O)CH(. )OH. The relative importances of the competing rearrangements in such cases is estimated by assuming they are approximately proportional to the estimated OH abstracting rate constant from the H-donating group (Carter, 1999b). Based on this, the overall reaction is estimated to be OH + 0.04 HOCH <sub>2</sub> C(O)CH <sub>2</sub> . + 0.96 CH <sub>3</sub> C(O)CH(. )OH, with the subsequent reactions of these radicals being derived by the general estimation methods (Carter, 1999a).
119	All the species represented by ISOPROD are assumed to have the same overall photolysis rate as used for methacrolein.
120	The PROD2 mechanism was derived by averaging mechanisms for CH <sub>3</sub> C(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH, CH <sub>3</sub> C(O)CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> OH, CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> C(O)CH <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> -C(O)CH <sub>2</sub> CH <sub>3</sub> , and CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> C(O)CH <sub>2</sub> CH <sub>3</sub> , which were taken as representative of the products formed from VOCs measured in ambient air that are represented by PROD2 in the model (Carter, 1999). The mechanisms for these five representative PROD2 compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).
121	Assumed to photolyze with the same rate absorption cross section as used for MEK and other higher ketones. The overall quantum yield is assumed to be the same as that which gives best fits to chamber data for 2-heptanone (Carter et al, 1999e), which has the approximately the same number of carbons as the average for the set of compounds used to derive the PROD2 mechanism.
122	The RNO3 mechanism was derived by averaging mechanisms for CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ONO <sub>2</sub> , CH <sub>3</sub> CH(ONO <sub>2</sub> )CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH-(ONO <sub>2</sub> )CH <sub>2</sub> OH, CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> )(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub> , and CH <sub>3</sub> CH <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> , which were taken as representative of the products formed from VOCs

Table 47 (continued)

No.	Note
	measured in ambient air that are represented by RNO <sub>3</sub> in the model (Carter, 1999). The mechanisms for these three representative RNO <sub>3</sub> compounds were derived using the mechanism generation and estimation methods discussed by Carter (1999).
123	Absorption cross sections given by IUPAC (Atkinson et al, 1997a, 1999) for isopropyl nitrate are used. As discussed by IUPAC (Atkinson et al, 1999), the quantum yield is expected to be near unity for formation of NO <sub>2</sub> .
124	DCB1 is used to represent aromatic ring fragmentation products that do not undergo significant photodecomposition to radicals. Its mechanism is largely parameterized, but it is based roughly on that expected for unsaturated dicarbonyls such as 2-butene-1,3-dial.
125	The rate constant is based on data of Bierbach et al (1994). The reaction is assumed to proceed via addition of OH to double bond, followed by decomposition of the alkoxy radical to HCO and HC(O)CH(OH)CHO, where the latter is represented by RCHO. Although this mechanism may not be what one would estimate for the non-photoreactive unsaturated diketones (Bierbach et al, 1994; Tuazon et al, ??) expected to be formed from o-substituted aromatics, best fits to the o-xylene and 1,2,4-trimethylbenzene chamber data are obtained if this mechanism is used.
126	The photolysis action spectra of these products are assumed to be similar to that for acrolein, so the absorption cross sections of acrolein are used, with a wavelength-independent overall quantum yield. The overall quantum yield is adjusted to optimize fits of model simulations to the benzene - NO <sub>x</sub> experiments used in the optimization of the previous version of the mechanism by Carter et al (1997a). The photolysis mechanism is represented as being similar to that used for DCB2 and DCB3. However, best fits to benzene - NO <sub>x</sub> experiments are obtained if this photolysis is assumed to be slow, so the reaction is not included in the mechanism.
127	The rate constant is based on the data of Bierbach et al (1994). The reaction is assumed to involve initial formation of glyoxal and HC(O)CHO <sub>2</sub> .
128	DCB2 and DCB3 represent the highly photoreactive unsaturated dicarbonyl product formed from the ring-opening reactions of the alkylbenzenes. To fit chamber data using differing light sources, they are represented by two species, which differ only in their action spectra and overall quantum yields, with the action spectrum of DCB2 being like methyl glyoxal, and that of DCB3 being like acrolein, and with the overall quantum yields adjusted separately to fit chamber data. Its reactions are based roughly on estimated reactions of a 5-carbon compound with general structure XC(O)CX=CXC(O)X, where X can be H or alkyl.
129	Assumed to have the same rate constant as used for DCB1. Mechanism represented as OH adding to double bond in XC(O)CX=CXC(O)X, with alkoxy radical decomposing to CH <sub>3</sub> CO. and XCO-CH(OH)-CXO, the latter being represented by RCHO. Note that the general alkoxy radical estimation method (Carter, 1999) predicts that alkoxy radicals like RCH(OH)CH(O.)C(O)R' will decompose primarily to RCH(OH)CHO + RC(O).
130	The overall quantum yields for DCB2 and DCB3 were optimized to give best fits of model simulations of NO oxidation, O <sub>3</sub> formation and xylene consumption in m-xylene - NO <sub>x</sub> chamber runs with various light sources, and also to mini-surrogate - NO <sub>x</sub> runs. The DCB2 and DCB3 quantum yields had to be adjusted as well as the yields of these products from m-xylene to best fit the data for the various light sources, and also to fit the results of the mini-surrogate as well as the



Table 47 (continued)

No.	Note
	m-xylene only runs. (For the other aromatics, only the DCB2 and DCB3 yields are optimized.) The photolysis mechanisms are unknown, and probably highly variable depending on the species involved. For an $\text{RC(O)CH=CHC(O)H}$ structure, the most energetically favored initial reaction is formation of $\text{R} \cdot + \text{HCOCH=CHCO} \cdot$ , but assuming that mechanism results in a model that consistently underpredicts PAN yields in alkylbenzene - $\text{NO}_x$ chamber experiments. Therefore, a set of products is assumed to be formed that may result from various different reaction
131	Isoprene mechanism used is based on the "four product" condensed isoprene mechanism of Carter (1996) which in turn is based on the detailed isoprene mechanism of Carter and Atkinson (1996). The rate constants and the major initial reaction pathways are the same as used in those mechanisms. Some minor changes in product yields resulted in some cases from use of the general mechanism estimation system (Carter, 1999a) to generate the overall reaction schemes, or as indicated in other footnotes.
132	The overall nitrate yield is slightly higher than the adjusted nitrate yields in the Carter and Atkinson (1996) mechanism because the mechanism generation system included some nitrate formation from peroxy radicals formed in secondary reactions. Although the yields were not readjusted, the mechanism still gives satisfactory fits to the isoprene chamber data used in the nitrate yield adjustments by Carter and Atkinson (1996).
133	The excited $\text{CH}_2=\text{CHC}(\text{O}_2)\text{CH}_3$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}_2 \cdot$ biradical reactions are the same as given by Carter and Atkinson (1996), except that the $\text{CH}_2=\text{CHC}(\text{O})\text{O}_2 \cdot$ formed from the former is represented by MA-RCO3, and the propene formed from the latter is represented by PROD2.
134	All the organic products formed in this reaction are represented by ISOPROD. A small amount of nitrate formation is estimated to occur from the reactions of the substituted peroxy radicals with NO (Carter, 1999a).
135	PROD2 is used to represent the various isoprene oxide products. And MA-RCO3 is used to represent $\text{CH}_2=\text{CHC}(\text{O})\text{OO} \cdot$ . Note that this mechanism, which is based on that of Carter and Atkinson (1996) is inconsistent with the mechanisms for the reactions of $\text{O}^3\text{P}$ with the other higher alkenes, which are assumed not to form radical products. However, assuming no radical formation in the reaction of $\text{O}^3\text{P}$ with isoprene results in somewhat degraded model performance in simulations of the results of the isoprene experiments discussed by Carter and Atkinson (1996).

Table 48. Listing of the absorption cross sections and quantum yields for the photolysis reactions.

WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
NO2														
205.0	4.31e-19	1.000	210.0	4.72e-19	1.000	215.0	4.95e-19	1.000	220.0	4.56e-19	1.000	225.0	3.79e-19	1.000
230.0	2.74e-19	1.000	235.0	1.67e-19	1.000	240.0	9.31e-20	1.000	245.0	4.74e-20	1.000	250.0	2.48e-20	1.000
255.0	1.95e-20	1.000	260.0	2.24e-20	1.000	265.0	2.73e-20	1.000	270.0	4.11e-20	1.000	275.0	4.90e-20	1.000
280.0	5.92e-20	1.000	285.0	7.39e-20	1.000	290.0	9.00e-20	1.000	295.0	1.09e-19	1.000	300.0	1.31e-19	1.000
305.0	1.57e-19	1.000	310.0	1.86e-19	1.000	315.0	2.15e-19	0.990	320.0	2.48e-19	0.990	325.0	2.81e-19	0.990
330.0	3.13e-19	0.990	335.0	3.43e-19	0.990	340.0	3.80e-19	0.990	345.0	4.07e-19	0.990	350.0	4.31e-19	0.990
355.0	4.72e-19	0.990	360.0	4.83e-19	0.980	365.0	5.17e-19	0.980	370.0	5.32e-19	0.980	375.0	5.51e-19	0.980
380.0	5.64e-19	0.970	385.0	5.76e-19	0.970	390.0	5.93e-19	0.960	395.0	5.85e-19	0.935	400.0	6.02e-19	0.820
405.0	5.78e-19	0.355	410.0	6.00e-19	0.130	411.0	5.93e-19	0.110	412.0	5.86e-19	0.094	413.0	5.79e-19	0.083
414.0	5.72e-19	0.070	415.0	5.65e-19	0.059	416.0	5.68e-19	0.048	417.0	5.71e-19	0.039	418.0	5.75e-19	0.030
419.0	5.78e-19	0.023	420.0	5.81e-19	0.018	421.0	5.72e-19	0.012	422.0	5.64e-19	0.008	423.0	5.55e-19	0.004
424.0	5.47e-19	0.000												
NO3NO														
585.0	2.89e-18	0.000	586.0	3.32e-18	0.050	587.0	4.16e-18	0.100	588.0	5.04e-18	0.150	589.0	6.13e-18	0.200
590.0	5.96e-18	0.250	591.0	5.44e-18	0.280	592.0	5.11e-18	0.310	593.0	4.58e-18	0.340	594.0	4.19e-18	0.370
595.0	4.29e-18	0.400	596.0	4.62e-18	0.370	597.0	4.36e-18	0.340	598.0	3.67e-18	0.310	599.0	3.10e-18	0.280
600.0	2.76e-18	0.250	601.0	2.86e-18	0.240	602.0	3.32e-18	0.230	603.0	3.80e-18	0.220	604.0	4.37e-18	0.210
605.0	4.36e-18	0.200	606.0	3.32e-18	0.200	607.0	2.40e-18	0.200	608.0	1.85e-18	0.200	609.0	1.71e-18	0.200
610.0	1.77e-18	0.200	611.0	1.91e-18	0.180	612.0	2.23e-18	0.160	613.0	2.63e-18	0.140	614.0	2.55e-18	0.120
615.0	2.26e-18	0.100	616.0	2.09e-18	0.100	617.0	2.11e-18	0.100	618.0	2.39e-18	0.100	619.0	2.56e-18	0.100
620.0	3.27e-18	0.100	621.0	5.24e-18	0.090	622.0	1.02e-17	0.080	623.0	1.47e-17	0.070	624.0	1.21e-17	0.060
625.0	8.38e-18	0.050	626.0	7.30e-18	0.050	627.0	7.53e-18	0.050	628.0	7.37e-18	0.050	629.0	6.98e-18	0.050
630.0	6.76e-18	0.050	631.0	4.84e-18	0.046	632.0	3.27e-18	0.042	633.0	2.17e-18	0.038	634.0	1.64e-18	0.034
635.0	1.44e-18	0.030	636.0	1.69e-18	0.024	637.0	2.07e-18	0.018	638.0	2.03e-18	0.012	639.0	1.58e-18	0.006
640.0	1.23e-18	0.000												
NO3NO2														
400.0	0.00e+00	1.000	401.0	0.00e+00	1.000	402.0	0.00e+00	1.000	403.0	2.00e-20	1.000	404.0	0.00e+00	1.000
405.0	3.00e-20	1.000	406.0	2.00e-20	1.000	407.0	1.00e-20	1.000	408.0	3.00e-20	1.000	409.0	0.00e+00	1.000
410.0	1.00e-20	1.000	411.0	2.00e-20	1.000	412.0	5.00e-20	1.000	413.0	5.00e-20	1.000	414.0	2.00e-20	1.000
415.0	6.00e-20	1.000	416.0	6.00e-20	1.000	417.0	7.00e-20	1.000	418.0	5.00e-20	1.000	419.0	8.00e-20	1.000
420.0	8.00e-20	1.000	421.0	8.00e-20	1.000	422.0	9.00e-20	1.000	423.0	1.10e-19	1.000	424.0	9.00e-20	1.000
425.0	7.00e-20	1.000	426.0	1.40e-19	1.000	427.0	1.40e-19	1.000	428.0	1.20e-19	1.000	429.0	1.10e-19	1.000
430.0	1.70e-19	1.000	431.0	1.30e-19	1.000	432.0	1.50e-19	1.000	433.0	1.80e-19	1.000	434.0	1.80e-19	1.000
435.0	1.60e-19	1.000	436.0	1.50e-19	1.000	437.0	1.80e-19	1.000	438.0	2.10e-19	1.000	439.0	2.00e-19	1.000
440.0	1.90e-19	1.000	441.0	1.80e-19	1.000	442.0	2.10e-19	1.000	443.0	1.80e-19	1.000	444.0	1.90e-19	1.000
445.0	2.00e-19	1.000	446.0	2.40e-19	1.000	447.0	2.90e-19	1.000	448.0	2.40e-19	1.000	449.0	2.80e-19	1.000
450.0	2.90e-19	1.000	451.0	3.00e-19	1.000	452.0	3.30e-19	1.000	453.0	3.10e-19	1.000	454.0	3.60e-19	1.000
455.0	3.60e-19	1.000	456.0	3.60e-19	1.000	457.0	4.00e-19	1.000	458.0	3.70e-19	1.000	459.0	4.20e-19	1.000
460.0	4.00e-19	1.000	461.0	3.90e-19	1.000	462.0	4.00e-19	1.000	463.0	4.10e-19	1.000	464.0	4.80e-19	1.000
465.0	5.10e-19	1.000	466.0	5.40e-19	1.000	467.0	5.70e-19	1.000	468.0	5.60e-19	1.000	469.0	5.80e-19	1.000
470.0	5.90e-19	1.000	471.0	6.20e-19	1.000	472.0	6.40e-19	1.000	473.0	6.20e-19	1.000	474.0	6.20e-19	1.000
475.0	6.80e-19	1.000	476.0	7.80e-19	1.000	477.0	7.70e-19	1.000	478.0	7.30e-19	1.000	479.0	7.30e-19	1.000
480.0	7.00e-19	1.000	481.0	7.10e-19	1.000	482.0	7.10e-19	1.000	483.0	7.20e-19	1.000	484.0	7.70e-19	1.000
485.0	8.20e-19	1.000	486.0	9.10e-19	1.000	487.0	9.20e-19	1.000	488.0	9.50e-19	1.000	489.0	9.60e-19	1.000
490.0	1.03e-18	1.000	491.0	9.90e-19	1.000	492.0	9.90e-19	1.000	493.0	1.01e-18	1.000	494.0	1.01e-18	1.000
495.0	1.06e-18	1.000	496.0	1.21e-18	1.000	497.0	1.22e-18	1.000	498.0	1.20e-18	1.000	499.0	1.17e-18	1.000
500.0	1.13e-18	1.000	501.0	1.11e-18	1.000	502.0	1.11e-18	1.000	503.0	1.11e-18	1.000	504.0	1.26e-18	1.000
505.0	1.28e-18	1.000	506.0	1.34e-18	1.000	507.0	1.28e-18	1.000	508.0	1.27e-18	1.000	509.0	1.35e-18	1.000
510.0	1.51e-18	1.000	511.0	1.73e-18	1.000	512.0	1.77e-18	1.000	513.0	1.60e-18	1.000	514.0	1.58e-18	1.000
515.0	1.58e-18	1.000	516.0	1.56e-18	1.000	517.0	1.49e-18	1.000	518.0	1.44e-18	1.000	519.0	1.54e-18	1.000
WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
520.0	1.68e-18	1.000	521.0	1.83e-18	1.000	522.0	1.93e-18	1.000	523.0	1.77e-18	1.000	524.0	1.64e-18	1.000
525.0	1.58e-18	1.000	526.0	1.63e-18	1.000	527.0	1.81e-18	1.000	528.0	2.10e-18	1.000	529.0	2.39e-18	1.000
530.0	2.23e-18	1.000	531.0	2.09e-18	1.000	532.0	2.02e-18	1.000	533.0	1.95e-18	1.000	534.0	2.04e-18	1.000
535.0	2.30e-18	1.000	536.0	2.57e-18	1.000	537.0	2.58e-18	1.000	538.0	2.34e-18	1.000	539.0	2.04e-18	1.000
540.0	2.10e-18	1.000	541.0	2.04e-18	1.000	542.0	1.88e-18	1.000	543.0	1.68e-18	1.000	544.0	1.70e-18	1.000

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
520.0	1.68e-18	1.000	521.0	1.83e-18	1.000	522.0	1.93e-18	1.000	523.0	1.77e-18	1.000	524.0	1.64e-18	1.000
525.0	1.58e-18	1.000	526.0	1.63e-18	1.000	527.0	1.81e-18	1.000	528.0	2.10e-18	1.000	529.0	2.39e-18	1.000
530.0	2.23e-18	1.000	531.0	2.09e-18	1.000	532.0	2.02e-18	1.000	533.0	1.95e-18	1.000	534.0	2.04e-18	1.000
535.0	2.30e-18	1.000	536.0	2.57e-18	1.000	537.0	2.58e-18	1.000	538.0	2.34e-18	1.000	539.0	2.04e-18	1.000
540.0	2.10e-18	1.000	541.0	2.04e-18	1.000	542.0	1.88e-18	1.000	543.0	1.68e-18	1.000	544.0	1.70e-18	1.000
545.0	1.96e-18	1.000	546.0	2.42e-18	1.000	547.0	2.91e-18	1.000	548.0	2.98e-18	1.000	549.0	2.71e-18	1.000
550.0	2.48e-18	1.000	551.0	2.43e-18	1.000	552.0	2.47e-18	1.000	553.0	2.53e-18	1.000	554.0	2.78e-18	1.000
555.0	3.11e-18	1.000	556.0	3.26e-18	1.000	557.0	3.29e-18	1.000	558.0	3.51e-18	1.000	559.0	3.72e-18	1.000
560.0	3.32e-18	1.000	561.0	2.98e-18	1.000	562.0	2.90e-18	1.000	563.0	2.80e-18	1.000	564.0	2.72e-18	1.000
565.0	2.73e-18	1.000	566.0	2.85e-18	1.000	567.0	2.81e-18	1.000	568.0	2.85e-18	1.000	569.0	2.89e-18	1.000
570.0	2.79e-18	1.000	571.0	2.76e-18	1.000	572.0	2.74e-18	1.000	573.0	2.78e-18	1.000	574.0	2.86e-18	1.000
575.0	3.08e-18	1.000	576.0	3.27e-18	1.000	577.0	3.38e-18	1.000	578.0	3.31e-18	1.000	579.0	3.24e-18	1.000
580.0	3.34e-18	1.000	581.0	3.55e-18	1.000	582.0	3.28e-18	1.000	583.0	2.93e-18	1.000	584.0	2.82e-18	1.000
585.0	2.39e-18	1.000	586.0	3.32e-18	0.950	587.0	4.16e-18	0.900	588.0	5.04e-18	0.850	589.0	6.13e-18	0.800
590.0	5.96e-18	0.750	591.0	5.44e-18	0.720	592.0	5.11e-18	0.690	593.0	4.58e-18	0.660	594.0	4.19e-18	0.630
595.0	4.29e-18	0.600	596.0	4.62e-18	0.590	597.0	4.36e-18	0.580	598.0	3.67e-18	0.570	599.0	3.10e-18	0.560
600.0	2.76e-18	0.550	601.0	2.86e-18	0.540	602.0	3.32e-18	0.530	603.0	3.80e-18	0.520	604.0	4.37e-18	0.510
605.0	4.36e-18	0.400	606.0	3.32e-18	0.380	607.0	2.40e-18	0.360	608.0	1.85e-18	0.340	609.0	1.71e-18	0.320
610.0	1.77e-18	0.300	611.0	1.91e-18	0.290	612.0	2.23e-18	0.280	613.0	2.63e-18	0.270	614.0	2.55e-18	0.260
615.0	2.26e-18	0.250	616.0	2.09e-18	0.240	617.0	2.11e-18	0.230	618.0	2.39e-18	0.220	619.0	2.56e-18	0.210
620.0	3.27e-18	0.200	621.0	5.24e-18	0.190	622.0	1.02e-17	0.180	623.0	1.47e-17	0.170	624.0	1.21e-17	0.160
625.0	8.38e-18	0.150	626.0	7.30e-18	0.130	627.0	7.53e-18	0.110	628.0	7.37e-18	0.090	629.0	6.98e-18	0.070
630.0	6.76e-18	0.050	631.0	4.84e-18	0.040	632.0	3.27e-18	0.030	633.0	2.17e-18	0.020	634.0	1.64e-18	0.010
635.0	1.44e-18	0.000												
O3O3P														
175.4	8.11e-19	0.050	177.0	8.11e-19	0.050	178.6	7.99e-19	0.050	180.2	7.86e-19	0.050	181.8	7.63e-19	0.050
183.5	7.29e-19	0.050	185.2	6.88e-19	0.050	186.9	6.22e-19	0.050	188.7	5.76e-19	0.050	190.5	5.26e-19	0.050
192.3	4.76e-19	0.050	194.2	4.28e-19	0.050	196.1	3.83e-19	0.050	198.0	3.47e-19	0.050	200.0	3.23e-19	0.050
202.0	3.14e-19	0.050	204.1	3.26e-19	0.050	206.2	3.64e-19	0.050	208.3	4.34e-19	0.050	210.5	5.42e-19	0.050
212.8	6.99e-19	0.050	215.0	9.20e-19	0.050	217.4	1.19e-18	0.050	219.8	1.55e-18	0.050	222.2	1.99e-18	0.050
224.7	2.56e-18	0.050	227.3	3.23e-18	0.050	229.9	4.00e-18	0.050	232.6	4.83e-18	0.050	235.3	5.79e-18	0.050
238.1	6.86e-18	0.050	241.0	7.97e-18	0.050	243.9	9.00e-18	0.050	246.9	1.00e-17	0.050	250.1	1.08e-17	0.050
253.2	1.13e-17	0.050	256.4	1.15e-17	0.050	259.7	1.12e-17	0.050	263.2	1.06e-17	0.050	266.7	9.65e-18	0.050
270.3	8.34e-18	0.050	274.0	6.92e-18	0.050	277.8	5.42e-18	0.050	281.7	4.02e-18	0.050	285.7	2.77e-18	0.050
289.9	1.79e-18	0.050	290.0	1.77e-18	0.050	294.1	1.09e-18	0.050	295.0	9.95e-19	0.050	298.5	6.24e-19	0.050
300.0	5.30e-19	0.050	303.0	3.43e-19	0.015	305.0	2.76e-19	0.020	306.0	2.42e-19	0.050	307.0	2.09e-19	0.123
307.7	1.85e-19	0.196	308.0	1.80e-19	0.227	309.0	1.61e-19	0.333	310.0	1.43e-19	0.400	311.0	1.25e-19	0.612
312.0	1.07e-19	0.697	312.5	9.80e-20	0.718	313.0	9.32e-20	0.738	314.0	8.36e-20	0.762	315.0	7.40e-20	0.765
316.0	6.44e-20	0.779	317.0	5.48e-20	0.791	317.5	5.00e-20	0.799	318.0	4.75e-20	0.806	319.0	4.25e-20	0.822
322.5	2.49e-20	0.906	327.5	1.20e-20	0.940	332.5	6.17e-21	0.950	337.5	2.74e-21	0.975	342.5	1.17e-21	1.000
347.5	5.90e-22	1.000	352.5	2.70e-22	1.000	357.5	1.10e-22	1.000	362.5	5.00e-23	1.000	367.5	0.00e+00	1.000
400.0	0.00e+00	1.000	410.0	1.20e-23	1.000	420.0	2.20e-23	1.000	440.0	1.12e-22	1.000	460.0	3.28e-22	1.000
480.0	6.84e-22	1.000	500.0	1.22e-21	1.000	520.0	1.82e-21	1.000	540.0	2.91e-21	1.000	560.0	3.94e-21	1.000
580.0	4.59e-21	1.000	600.0	5.11e-21	1.000	620.0	4.00e-21	1.000	640.0	2.96e-21	1.000	660.0	2.09e-21	1.000
680.0	1.36e-21	1.000	700.0	9.10e-22	1.000	750.0	3.20e-22	1.000	800.0	1.60e-22	1.000	900.0	0.00e+00	1.000

Table 48 (continued)

WL (nm)	Abs (cm <sup>-2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>-2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>-2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>-2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>-2</sup> )	QY (nm)
O3O1D														
175.4	8.11e-19	0.870	177.0	8.11e-19	0.870	178.6	7.99e-19	0.870	180.2	7.86e-19	0.870	181.8	7.63e-19	0.870
183.5	7.29e-19	0.870	185.2	6.88e-19	0.870	186.9	6.22e-19	0.870	188.7	5.76e-19	0.870	190.5	5.26e-19	0.870
192.3	4.76e-19	0.870	194.2	4.28e-19	0.870	196.1	3.83e-19	0.870	198.0	3.47e-19	0.870	200.0	3.23e-19	0.870
202.0	3.14e-19	0.870	204.1	3.26e-19	0.870	206.2	3.64e-19	0.870	208.3	4.34e-19	0.870	210.5	5.42e-19	0.870
212.8	6.99e-19	0.870	215.0	9.20e-19	0.870	217.4	1.19e-18	0.870	219.8	1.55e-18	0.870	222.2	1.99e-18	0.870
224.7	2.56e-18	0.870	227.3	3.23e-18	0.870	229.9	4.00e-18	0.870	232.6	4.83e-18	0.870	235.3	5.79e-18	0.870
238.1	6.86e-18	0.870	241.0	7.97e-18	0.870	243.9	9.00e-18	0.870	246.9	1.00e-17	0.870	250.1	1.08e-17	0.870
253.2	1.13e-17	0.870	256.4	1.15e-17	0.870	259.7	1.12e-17	0.870	263.2	1.06e-17	0.870	266.7	9.65e-18	0.870
270.3	8.34e-18	0.870	274.0	6.92e-18	0.881	277.8	5.42e-18	0.896	281.7	4.02e-18	0.911	285.7	2.77e-18	0.926
289.9	1.79e-18	0.942	290.0	1.77e-18	0.942	294.1	1.09e-18	0.950	295.0	9.95e-19	0.950	298.5	6.24e-19	0.950
300.0	5.30e-19	0.950	303.0	3.43e-19	0.985	305.0	2.76e-19	0.980	306.0	2.42e-19	0.950	307.0	2.09e-19	0.877
307.7	1.85e-19	0.804	308.0	1.80e-19	0.773	309.0	1.61e-19	0.667	310.0	1.43e-19	0.600	311.0	1.25e-19	0.388
312.0	1.07e-19	0.303	312.5	9.80e-20	0.283	313.0	9.32e-20	0.262	314.0	8.36e-20	0.238	315.0	7.40e-20	0.235
316.0	6.44e-20	0.221	317.0	5.48e-20	0.209	317.5	5.00e-20	0.202	318.0	4.75e-20	0.194	319.0	4.25e-20	0.178
322.5	2.49e-20	0.095	327.5	1.20e-20	0.060	332.5	6.17e-21	0.050	337.5	2.74e-21	0.025	342.5	1.17e-21	0.000
347.5	5.90e-22	0.000												
HONO-NO														
309.0	0.00e+00	0.410	310.0	1.30e-20	0.410	311.0	1.90e-20	0.411	312.0	2.80e-20	0.421	313.0	2.20e-20	0.432
314.0	3.60e-20	0.443	315.0	3.00e-20	0.454	316.0	1.40e-20	0.464	317.0	3.10e-20	0.475	318.0	5.60e-20	0.486
319.0	3.60e-20	0.496	320.0	4.90e-20	0.507	321.0	7.80e-20	0.518	322.0	4.90e-20	0.529	323.0	5.10e-20	0.539
324.0	7.10e-20	0.550	325.0	5.00e-20	0.561	326.0	2.90e-20	0.571	327.0	6.60e-20	0.582	328.0	1.17e-19	0.593
329.0	6.10e-20	0.604	330.0	1.11e-19	0.614	331.0	1.79e-19	0.625	332.0	8.70e-20	0.636	333.0	7.60e-20	0.646
334.0	9.60e-20	0.657	335.0	9.60e-20	0.668	336.0	7.20e-20	0.679	337.0	5.30e-20	0.689	338.0	1.00e-19	0.700
339.0	1.88e-19	0.711	340.0	1.00e-19	0.721	341.0	1.70e-19	0.732	342.0	3.86e-19	0.743	343.0	1.49e-19	0.754
344.0	9.70e-20	0.764	345.0	1.09e-19	0.775	346.0	1.23e-19	0.786	347.0	1.04e-19	0.796	348.0	9.10e-20	0.807
349.0	7.90e-20	0.818	350.0	1.12e-19	0.829	351.0	2.12e-19	0.839	352.0	1.55e-19	0.850	353.0	1.91e-19	0.861
354.0	5.81e-19	0.871	355.0	3.64e-19	0.882	356.0	1.41e-19	0.893	357.0	1.17e-19	0.904	358.0	1.20e-19	0.914
359.0	1.04e-19	0.925	360.0	9.00e-20	0.936	361.0	8.30e-20	0.946	362.0	8.00e-20	0.957	363.0	9.60e-20	0.968
364.0	1.46e-19	0.979	365.0	1.68e-19	0.989	366.0	1.83e-19	1.000	367.0	3.02e-19	1.000	368.0	5.20e-19	1.000
369.0	3.88e-19	1.000	370.0	1.78e-19	1.000	371.0	1.13e-19	1.000	372.0	1.00e-19	1.000	373.0	7.70e-20	1.000
374.0	6.20e-20	1.000	375.0	5.30e-20	1.000	376.0	5.30e-20	1.000	377.0	5.00e-20	1.000	378.0	5.80e-20	1.000
379.0	8.00e-20	1.000	380.0	9.60e-20	1.000	381.0	1.13e-19	1.000	382.0	1.59e-19	1.000	383.0	2.10e-19	1.000
384.0	2.41e-19	1.000	385.0	2.03e-19	1.000	386.0	1.34e-19	1.000	387.0	9.00e-20	1.000	388.0	5.60e-20	1.000
389.0	3.40e-20	1.000	390.0	2.70e-20	1.000	391.0	2.00e-20	1.000	392.0	1.50e-20	1.000	393.0	1.10e-20	1.000
394.0	6.00e-21	1.000	395.0	1.00e-20	1.000	396.0	4.00e-21	1.000	400.0	0.00e+00	1.000			
HONO-NO2														
309.0	0.00e+00	0.590	310.0	1.30e-20	0.590	311.0	1.90e-20	0.589	312.0	2.80e-20	0.579	313.0	2.20e-20	0.568
314.0	3.60e-20	0.557	315.0	3.00e-20	0.546	316.0	1.40e-20	0.536	317.0	3.10e-20	0.525	318.0	5.60e-20	0.514
319.0	3.60e-20	0.504	320.0	4.90e-20	0.493	321.0	7.80e-20	0.482	322.0	4.90e-20	0.471	323.0	5.10e-20	0.461
324.0	7.10e-20	0.450	325.0	5.00e-20	0.439	326.0	2.90e-20	0.429	327.0	6.60e-20	0.418	328.0	1.17e-19	0.407
329.0	6.10e-20	0.396	330.0	1.11e-19	0.386	331.0	1.79e-19	0.375	332.0	8.70e-20	0.364	333.0	7.60e-20	0.354
334.0	9.60e-20	0.343	335.0	9.60e-20	0.332	336.0	7.20e-20	0.321	337.0	5.30e-20	0.311	338.0	1.00e-19	0.300
339.0	1.88e-19	0.289	340.0	1.00e-19	0.279	341.0	1.70e-19	0.268	342.0	3.86e-19	0.257	343.0	1.49e-19	0.246
344.0	9.70e-20	0.236	345.0	1.09e-19	0.225	346.0	1.23e-19	0.214	347.0	1.04e-19	0.204	348.0	9.10e-20	0.193
349.0	7.90e-20	0.182	350.0	1.12e-19	0.171	351.0	2.12e-19	0.161	352.0	1.55e-19	0.150	353.0	1.91e-19	0.139
354.0	5.81e-19	0.129	355.0	3.64e-19	0.118	356.0	1.41e-19	0.107	357.0	1.17e-19	0.096	358.0	1.20e-19	0.086
359.0	1.04e-19	0.075	360.0	9.00e-20	0.064	361.0	8.30e-20	0.054	362.0	8.00e-20	0.043	363.0	9.60e-20	0.032
364.0	1.46e-19	0.021	365.0	1.68e-19	0.011	366.0	1.83e-19	0.000						

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
HNO3														
190.0	1.36e-17	1.000	195.0	1.02e-17	1.000	200.0	5.88e-18	1.000	205.0	2.80e-18	1.000	210.0	1.04e-18	1.000
215.0	3.65e-19	1.000	220.0	1.49e-19	1.000	225.0	8.81e-20	1.000	230.0	5.75e-20	1.000	235.0	3.75e-20	1.000
240.0	2.58e-20	1.000	245.0	2.11e-20	1.000	250.0	1.97e-20	1.000	255.0	1.95e-20	1.000	260.0	1.91e-20	1.000
265.0	1.80e-20	1.000	270.0	1.62e-20	1.000	275.0	1.38e-20	1.000	280.0	1.12e-20	1.000	285.0	8.58e-21	1.000
290.0	6.15e-21	1.000	295.0	4.12e-21	1.000	300.0	2.63e-21	1.000	305.0	1.50e-21	1.000	310.0	8.10e-22	1.000
315.0	4.10e-22	1.000	320.0	2.00e-22	1.000	325.0	9.50e-23	1.000	330.0	4.30e-23	1.000	335.0	2.20e-23	1.000
340.0	1.00e-23	1.000	345.0	6.00e-24	1.000	350.0	4.00e-24	1.000	355.0	0.00e+00	1.000			
HO2NO2														
190.0	1.01e-17	1.000	195.0	8.16e-18	1.000	200.0	5.63e-18	1.000	205.0	3.67e-18	1.000	210.0	2.39e-18	1.000
215.0	1.61e-18	1.000	220.0	1.18e-18	1.000	225.0	9.32e-19	1.000	230.0	7.88e-19	1.000	235.0	6.80e-19	1.000
240.0	5.79e-19	1.000	245.0	4.97e-19	1.000	250.0	4.11e-19	1.000	255.0	3.49e-19	1.000	260.0	2.84e-19	1.000
265.0	2.29e-19	1.000	270.0	1.80e-19	1.000	275.0	1.33e-19	1.000	280.0	9.30e-20	1.000	285.0	6.20e-20	1.000
290.0	3.90e-20	1.000	295.0	2.40e-20	1.000	300.0	1.40e-20	1.000	305.0	8.50e-21	1.000	310.0	5.30e-21	1.000
315.0	3.90e-21	1.000	320.0	2.40e-21	1.000	325.0	1.50e-21	1.000	330.0	9.00e-22	1.000	335.0	0.00e+00	1.000
H2O2														
190.0	6.72e-19	1.000	195.0	5.63e-19	1.000	200.0	4.75e-19	1.000	205.0	4.08e-19	1.000	210.0	3.57e-19	1.000
215.0	3.07e-19	1.000	220.0	2.58e-19	1.000	225.0	2.17e-19	1.000	230.0	1.82e-19	1.000	235.0	1.50e-19	1.000
240.0	1.24e-19	1.000	245.0	1.02e-19	1.000	250.0	8.30e-20	1.000	255.0	6.70e-20	1.000	260.0	5.30e-20	1.000
265.0	4.20e-20	1.000	270.0	3.30e-20	1.000	275.0	2.60e-20	1.000	280.0	2.00e-20	1.000	285.0	1.50e-20	1.000
290.0	1.20e-20	1.000	295.0	9.00e-21	1.000	300.0	6.80e-21	1.000	305.0	5.10e-21	1.000	310.0	3.90e-21	1.000
315.0	2.90e-21	1.000	320.0	2.20e-21	1.000	325.0	1.60e-21	1.000	330.0	1.30e-21	1.000	335.0	1.00e-21	1.000
340.0	7.00e-22	1.000	345.0	5.00e-22	1.000	350.0	4.00e-22	1.000	355.0	0.00e+00	1.000			
HCHO_R														
240.0	6.40e-22	0.270	241.0	5.60e-22	0.272	242.0	1.05e-21	0.274	243.0	1.15e-21	0.276	244.0	8.20e-22	0.278
245.0	1.03e-21	0.280	246.0	9.80e-22	0.282	247.0	1.35e-21	0.284	248.0	1.91e-21	0.286	249.0	2.82e-21	0.288
250.0	2.05e-21	0.290	251.0	1.70e-21	0.291	252.0	2.88e-21	0.292	253.0	2.55e-21	0.293	254.0	2.55e-21	0.294
255.0	3.60e-21	0.295	256.0	5.09e-21	0.296	257.0	3.39e-21	0.297	258.0	2.26e-21	0.298	259.0	5.04e-21	0.299
260.0	5.05e-21	0.300	261.0	5.49e-21	0.308	262.0	5.20e-21	0.316	263.0	9.33e-21	0.324	264.0	8.23e-21	0.332
265.0	4.30e-21	0.340	266.0	4.95e-21	0.348	267.0	1.24e-20	0.356	268.0	1.11e-20	0.364	269.0	8.78e-21	0.372
270.0	9.36e-21	0.380	271.0	1.79e-20	0.399	272.0	1.23e-20	0.418	273.0	6.45e-21	0.437	274.0	6.56e-21	0.456
275.0	2.23e-20	0.475	276.0	2.42e-20	0.494	277.0	1.40e-20	0.513	278.0	1.05e-20	0.532	279.0	2.55e-20	0.551
280.0	2.08e-20	0.570	281.0	1.48e-20	0.586	282.0	8.81e-21	0.602	283.0	1.07e-20	0.618	284.0	4.49e-20	0.634
285.0	3.59e-20	0.650	286.0	1.96e-20	0.666	287.0	1.30e-20	0.682	288.0	3.36e-20	0.698	289.0	2.84e-20	0.714
290.0	1.30e-20	0.730	291.0	1.75e-20	0.735	292.0	8.32e-21	0.740	293.0	3.73e-20	0.745	294.0	6.54e-20	0.750
295.0	3.95e-20	0.755	296.0	2.33e-20	0.760	297.0	1.51e-20	0.765	298.0	4.04e-20	0.770	299.0	2.87e-20	0.775
300.0	8.71e-21	0.780	301.0	1.72e-20	0.780	302.0	1.06e-20	0.780	303.0	3.20e-20	0.780	304.0	6.90e-20	0.780
305.0	4.91e-20	0.780	306.0	4.63e-20	0.780	307.0	2.10e-20	0.780	308.0	1.49e-20	0.780	309.0	3.41e-20	0.780
310.0	1.95e-20	0.780	311.0	5.21e-21	0.764	312.0	1.12e-20	0.748	313.0	1.12e-20	0.732	314.0	4.75e-20	0.716
315.0	5.25e-20	0.700	316.0	2.90e-20	0.684	317.0	5.37e-20	0.668	318.0	2.98e-20	0.652	319.0	9.18e-21	0.636
320.0	1.26e-20	0.620	321.0	1.53e-20	0.585	322.0	6.69e-21	0.550	323.0	3.45e-21	0.515	324.0	8.16e-21	0.480
325.0	1.85e-20	0.445	326.0	5.95e-20	0.410	327.0	3.49e-20	0.375	328.0	1.09e-20	0.340	329.0	3.35e-20	0.305
330.0	3.32e-20	0.270	331.0	1.07e-20	0.243	332.0	2.89e-21	0.216	333.0	2.15e-21	0.189	334.0	1.71e-21	0.162
335.0	1.43e-21	0.135	336.0	1.94e-21	0.108	337.0	4.17e-21	0.081	338.0	2.36e-20	0.054	339.0	4.71e-20	0.027
340.0	2.48e-20	0.000												

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
HCHO_M														
240.0	6.40e-22	0.490	241.0	5.60e-22	0.490	242.0	1.05e-21	0.490	243.0	1.15e-21	0.490	244.0	8.20e-22	0.490
245.0	1.03e-21	0.490	246.0	9.80e-22	0.490	247.0	1.35e-21	0.490	248.0	1.91e-21	0.490	249.0	2.82e-21	0.490
250.0	2.05e-21	0.490	251.0	1.70e-21	0.490	252.0	2.88e-21	0.490	253.0	2.55e-21	0.490	254.0	2.55e-21	0.490
255.0	3.60e-21	0.490	256.0	5.09e-21	0.490	257.0	3.39e-21	0.490	258.0	2.26e-21	0.490	259.0	5.04e-21	0.490
260.0	5.05e-21	0.490	261.0	5.49e-21	0.484	262.0	5.20e-21	0.478	263.0	9.33e-21	0.472	264.0	8.23e-21	0.466
265.0	4.30e-21	0.460	266.0	4.95e-21	0.454	267.0	1.24e-20	0.448	268.0	1.11e-20	0.442	269.0	8.78e-21	0.436
270.0	9.36e-21	0.430	271.0	1.79e-20	0.419	272.0	1.23e-20	0.408	273.0	6.45e-21	0.397	274.0	6.56e-21	0.386
275.0	2.23e-20	0.375	276.0	2.42e-20	0.364	277.0	1.40e-20	0.353	278.0	1.05e-20	0.342	279.0	2.55e-20	0.331
280.0	2.08e-20	0.320	281.0	1.48e-20	0.312	282.0	8.81e-21	0.304	283.0	1.07e-20	0.296	284.0	4.49e-20	0.288
285.0	3.59e-20	0.280	286.0	1.96e-20	0.272	287.0	1.30e-20	0.264	288.0	3.36e-20	0.256	289.0	2.84e-20	0.248
290.0	1.30e-20	0.240	291.0	1.75e-20	0.237	292.0	8.32e-21	0.234	293.0	3.73e-20	0.231	294.0	6.54e-20	0.228
295.0	3.95e-20	0.225	296.0	2.33e-20	0.222	297.0	1.51e-20	0.219	298.0	4.04e-20	0.216	299.0	2.87e-20	0.213
300.0	8.71e-21	0.210	301.0	1.72e-20	0.211	302.0	1.06e-20	0.212	303.0	3.20e-20	0.213	304.0	6.90e-20	0.214
305.0	4.91e-20	0.215	306.0	4.63e-20	0.216	307.0	2.10e-20	0.217	308.0	1.49e-20	0.218	309.0	3.41e-20	0.219
310.0	1.95e-20	0.220	311.0	5.21e-21	0.236	312.0	1.12e-20	0.252	313.0	1.12e-20	0.268	314.0	4.75e-20	0.284
315.0	5.25e-20	0.300	316.0	2.90e-20	0.316	317.0	5.37e-20	0.332	318.0	2.98e-20	0.348	319.0	9.18e-21	0.364
320.0	1.26e-20	0.380	321.0	1.53e-20	0.408	322.0	6.69e-21	0.436	323.0	3.45e-21	0.464	324.0	8.16e-21	0.492
325.0	1.85e-20	0.520	326.0	5.95e-20	0.548	327.0	3.49e-20	0.576	328.0	1.09e-20	0.604	329.0	3.35e-20	0.632
330.0	3.32e-20	0.660	331.0	1.07e-20	0.650	332.0	2.89e-21	0.640	333.0	2.15e-21	0.630	334.0	1.71e-21	0.620
335.0	1.43e-21	0.610	336.0	1.94e-21	0.600	337.0	4.17e-21	0.590	338.0	2.36e-20	0.580	339.0	4.71e-20	0.570
340.0	2.48e-20	0.560	341.0	7.59e-21	0.525	342.0	6.81e-21	0.490	343.0	1.95e-20	0.455	344.0	1.14e-20	0.420
345.0	3.23e-21	0.385	346.0	1.13e-21	0.350	347.0	6.60e-22	0.315	348.0	1.22e-21	0.280	349.0	3.20e-22	0.245
350.0	3.80e-22	0.210	351.0	1.04e-21	0.192	352.0	7.13e-21	0.174	353.0	2.21e-20	0.156	354.0	1.54e-20	0.138
355.0	6.76e-21	0.120	356.0	1.35e-21	0.102	357.0	3.60e-22	0.084	358.0	5.70e-23	0.066	359.0	5.80e-22	0.048
360.0	8.20e-22	0.000												
CCHO_R														
262.0	2.44e-20	0.326	266.0	3.05e-20	0.358	270.0	3.42e-20	0.390	274.0	4.03e-20	0.466	278.0	4.19e-20	0.542
280.0	4.50e-20	0.580	281.0	4.69e-20	0.575	282.0	4.72e-20	0.570	283.0	4.75e-20	0.565	284.0	4.61e-20	0.560
285.0	4.49e-20	0.555	286.0	4.44e-20	0.550	287.0	4.59e-20	0.545	288.0	4.72e-20	0.540	289.0	4.77e-20	0.535
290.0	4.89e-20	0.530	291.0	4.78e-20	0.520	292.0	4.68e-20	0.510	293.0	4.53e-20	0.500	294.0	4.33e-20	0.490
295.0	4.27e-20	0.480	296.0	4.24e-20	0.470	297.0	4.38e-20	0.460	298.0	4.41e-20	0.450	299.0	4.26e-20	0.440
300.0	4.16e-20	0.430	301.0	3.99e-20	0.418	302.0	3.86e-20	0.406	303.0	3.72e-20	0.394	304.0	3.48e-20	0.382
305.0	3.42e-20	0.370	306.0	3.42e-20	0.354	307.0	3.36e-20	0.338	308.0	3.33e-20	0.322	309.0	3.14e-20	0.306
310.0	2.93e-20	0.290	311.0	2.76e-20	0.266	312.0	2.53e-20	0.242	313.0	2.47e-20	0.218	314.0	2.44e-20	0.194
315.0	2.20e-20	0.170	316.0	2.04e-20	0.156	317.0	2.07e-20	0.142	318.0	1.98e-20	0.128	319.0	1.87e-20	0.114
320.0	1.72e-20	0.100	321.0	1.48e-20	0.088	322.0	1.40e-20	0.076	323.0	1.24e-20	0.064	324.0	1.09e-20	0.052
325.0	1.14e-20	0.040	326.0	1.07e-20	0.032	327.0	8.58e-21	0.024	328.0	7.47e-21	0.016	329.0	7.07e-21	0.008
C2CHO														
294.0	5.80e-20	0.890	295.0	5.57e-20	0.885	296.0	5.37e-20	0.880	297.0	5.16e-20	0.875	298.0	5.02e-20	0.870
299.0	5.02e-20	0.865	300.0	5.04e-20	0.860	301.0	5.09e-20	0.855	302.0	5.07e-20	0.850	303.0	4.94e-20	0.818
304.0	4.69e-20	0.786	305.0	4.32e-20	0.755	306.0	4.04e-20	0.723	307.0	3.81e-20	0.691	308.0	3.65e-20	0.659
309.0	3.62e-20	0.627	310.0	3.60e-20	0.596	311.0	3.53e-20	0.564	312.0	3.50e-20	0.532	313.0	3.32e-20	0.500
314.0	3.06e-20	0.480	315.0	2.77e-20	0.460	316.0	2.43e-20	0.440	317.0	2.18e-20	0.420	318.0	2.00e-20	0.400
319.0	1.86e-20	0.380	320.0	1.83e-20	0.360	321.0	1.78e-20	0.340	322.0	1.66e-20	0.320	323.0	1.58e-20	0.300
324.0	1.49e-20	0.280	325.0	1.30e-20	0.260	326.0	1.13e-20	0.248	327.0	9.96e-21	0.236	328.0	8.28e-21	0.223
329.0	6.85e-21	0.211	330.0	5.75e-21	0.199	331.0	4.94e-21	0.187	332.0	4.66e-21	0.174	333.0	4.30e-21	0.162
334.0	3.73e-21	0.150	335.0	3.25e-21	0.133	336.0	2.80e-21	0.117	337.0	2.30e-21	0.100	338.0	1.85e-21	0.083
339.0	1.66e-21	0.067	340.0	1.55e-21	0.050	341.0	1.19e-21	0.033	342.0	7.60e-22	0.017	343.0	4.50e-22	0.000

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
KETONE														
198.5	3.95e-19	1.000	199.0	1.61e-19	1.000	199.5	7.75e-20	1.000	200.0	3.76e-20	1.000	200.5	2.51e-20	1.000
201.0	1.83e-20	1.000	201.5	1.36e-20	1.000	202.0	1.16e-20	1.000	202.5	8.97e-21	1.000	203.0	4.62e-21	1.000
203.5	3.18e-21	1.000	204.0	2.42e-21	1.000	204.5	2.01e-21	1.000	205.0	1.77e-21	1.000	205.5	1.64e-21	1.000
206.0	1.54e-21	1.000	206.5	1.52e-21	1.000	207.0	1.54e-21	1.000	207.5	1.62e-21	1.000	208.0	1.64e-21	1.000
208.5	1.60e-21	1.000	209.0	1.57e-21	1.000	209.5	1.49e-21	1.000	210.0	1.47e-21	1.000	210.5	1.52e-21	1.000
211.0	1.50e-21	1.000	211.5	1.62e-21	1.000	212.0	1.81e-21	1.000	212.5	2.10e-21	1.000	213.0	2.23e-21	1.000
213.5	2.06e-21	1.000	214.0	1.69e-21	1.000	214.5	1.49e-21	1.000	215.0	1.42e-21	1.000	215.5	1.42e-21	1.000
216.0	1.42e-21	1.000	216.5	1.48e-21	1.000	217.0	1.48e-21	1.000	217.5	1.53e-21	1.000	218.0	1.56e-21	1.000
218.5	1.67e-21	1.000	219.0	1.68e-21	1.000	219.5	1.78e-21	1.000	220.0	1.85e-21	1.000	220.5	1.92e-21	1.000
221.0	2.01e-21	1.000	221.5	2.11e-21	1.000	222.0	2.23e-21	1.000	222.5	2.33e-21	1.000	223.0	2.48e-21	1.000
223.5	2.60e-21	1.000	224.0	2.74e-21	1.000	224.5	2.85e-21	1.000	225.0	3.04e-21	1.000	225.5	3.15e-21	1.000
226.0	3.33e-21	1.000	226.5	3.55e-21	1.000	227.0	3.73e-21	1.000	227.5	3.93e-21	1.000	228.0	4.11e-21	1.000
228.5	4.34e-21	1.000	229.0	4.56e-21	1.000	229.5	4.75e-21	1.000	230.0	5.01e-21	1.000	230.5	5.27e-21	1.000
231.0	5.53e-21	1.000	231.5	5.83e-21	1.000	232.0	6.15e-21	1.000	232.5	6.45e-21	1.000	233.0	6.73e-21	1.000
233.5	7.02e-21	1.000	234.0	7.42e-21	1.000	234.5	7.83e-21	1.000	235.0	8.11e-21	1.000	235.5	8.45e-21	1.000
236.0	8.82e-21	1.000	236.5	9.21e-21	1.000	237.0	9.65e-21	1.000	237.5	1.00e-20	1.000	238.0	1.05e-20	1.000
238.5	1.10e-20	1.000	239.0	1.15e-20	1.000	239.5	1.20e-20	1.000	240.0	1.23e-20	1.000	240.5	1.28e-20	1.000
241.0	1.32e-20	1.000	241.5	1.38e-20	1.000	242.0	1.44e-20	1.000	242.5	1.50e-20	1.000	243.0	1.57e-20	1.000
243.5	1.63e-20	1.000	244.0	1.68e-20	1.000	244.5	1.75e-20	1.000	245.0	1.81e-20	1.000	245.5	1.88e-20	1.000
246.0	1.96e-20	1.000	246.5	2.03e-20	1.000	247.0	2.11e-20	1.000	247.5	2.19e-20	1.000	248.0	2.25e-20	1.000
248.5	2.33e-20	1.000	249.0	2.40e-20	1.000	249.5	2.48e-20	1.000	250.0	2.56e-20	1.000	250.5	2.64e-20	1.000
251.0	2.73e-20	1.000	251.5	2.81e-20	1.000	252.0	2.88e-20	1.000	252.5	2.98e-20	1.000	253.0	3.07e-20	1.000
253.5	3.16e-20	1.000	254.0	3.25e-20	1.000	254.5	3.34e-20	1.000	255.0	3.43e-20	1.000	255.5	3.51e-20	1.000
256.0	3.59e-20	1.000	256.5	3.67e-20	1.000	257.0	3.75e-20	1.000	257.5	3.84e-20	1.000	258.0	3.94e-20	1.000
258.5	4.03e-20	1.000	259.0	4.13e-20	1.000	259.5	4.22e-20	1.000	260.0	4.28e-20	1.000	260.5	4.33e-20	1.000
261.0	4.41e-20	1.000	261.5	4.49e-20	1.000	262.0	4.57e-20	1.000	262.5	4.65e-20	1.000	263.0	4.72e-20	1.000
263.5	4.78e-20	1.000	264.0	4.85e-20	1.000	264.5	4.92e-20	1.000	265.0	4.99e-20	1.000	265.5	5.04e-20	1.000
266.0	5.12e-20	1.000	266.5	5.22e-20	1.000	267.0	5.28e-20	1.000	267.5	5.34e-20	1.000	268.0	5.41e-20	1.000
268.5	5.46e-20	1.000	269.0	5.51e-20	1.000	269.5	5.55e-20	1.000	270.0	5.59e-20	1.000	270.5	5.63e-20	1.000
271.0	5.66e-20	1.000	271.5	5.70e-20	1.000	272.0	5.74e-20	1.000	272.5	5.78e-20	1.000	273.0	5.81e-20	1.000
273.5	5.86e-20	1.000	274.0	5.90e-20	1.000	274.5	5.93e-20	1.000	275.0	5.96e-20	1.000	275.5	5.97e-20	1.000
276.0	5.98e-20	1.000	276.5	5.98e-20	1.000	277.0	5.99e-20	1.000	277.5	5.99e-20	1.000	278.0	5.98e-20	1.000
278.5	5.96e-20	1.000	279.0	5.96e-20	1.000	279.5	5.95e-20	1.000	280.0	5.94e-20	1.000	280.5	5.92e-20	1.000
281.0	5.90e-20	1.000	281.5	5.88e-20	1.000	282.0	5.86e-20	1.000	282.5	5.83e-20	1.000	283.0	5.79e-20	1.000
283.5	5.75e-20	1.000	284.0	5.71e-20	1.000	284.5	5.67e-20	1.000	285.0	5.61e-20	1.000	285.5	5.56e-20	1.000
286.0	5.51e-20	1.000	286.5	5.45e-20	1.000	287.0	5.41e-20	1.000	287.5	5.37e-20	1.000	288.0	5.33e-20	1.000
288.5	5.27e-20	1.000	289.0	5.21e-20	1.000	289.5	5.15e-20	1.000	290.0	5.08e-20	1.000	290.5	4.99e-20	1.000
291.0	4.89e-20	1.000	291.5	4.82e-20	1.000	292.0	4.73e-20	1.000	292.5	4.62e-20	1.000	293.0	4.53e-20	1.000
293.5	4.41e-20	1.000	294.0	4.32e-20	1.000	294.5	4.23e-20	1.000	295.0	4.15e-20	1.000	295.5	4.11e-20	1.000
296.0	4.01e-20	1.000	296.5	3.94e-20	1.000	297.0	3.88e-20	1.000	297.5	3.77e-20	1.000	298.0	3.69e-20	1.000
298.5	3.63e-20	1.000	299.0	3.54e-20	1.000	299.5	3.46e-20	1.000	300.0	3.36e-20	1.000	300.5	3.24e-20	1.000
301.0	3.16e-20	1.000	301.5	3.06e-20	1.000	302.0	2.95e-20	1.000	302.5	2.82e-20	1.000	303.0	2.70e-20	1.000
303.5	2.59e-20	1.000	304.0	2.49e-20	1.000	304.5	2.42e-20	1.000	305.0	2.34e-20	1.000	305.5	2.28e-20	1.000
306.0	2.19e-20	1.000	306.5	2.11e-20	1.000	307.0	2.04e-20	1.000	307.5	1.93e-20	1.000	308.0	1.88e-20	1.000
308.5	1.80e-20	1.000	309.0	1.73e-20	1.000	309.5	1.66e-20	1.000	310.0	1.58e-20	1.000	310.5	1.48e-20	1.000
311.0	1.42e-20	1.000	311.5	1.34e-20	1.000	312.0	1.26e-20	1.000	312.5	1.17e-20	1.000	313.0	1.13e-20	1.000
313.5	1.08e-20	1.000	314.0	1.04e-20	1.000	314.5	9.69e-21	1.000	315.0	8.91e-21	1.000	315.5	8.61e-21	1.000
316.0	7.88e-21	1.000	316.5	7.25e-21	1.000	317.0	6.92e-21	1.000	317.5	6.43e-21	1.000	318.0	6.07e-21	1.000
318.5	5.64e-21	1.000	319.0	5.19e-21	1.000	319.5	4.66e-21	1.000	320.0	4.36e-21	1.000	320.5	3.95e-21	1.000
321.0	3.64e-21	1.000	321.5	3.38e-21	1.000	322.0	3.17e-21	1.000	322.5	2.80e-21	1.000	323.0	2.62e-21	1.000

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
323.5	2.29e-21	1.000	324.0	2.13e-21	1.000	324.5	1.93e-21	1.000	325.0	1.70e-21	1.000	325.5	1.58e-21	1.000
326.0	1.48e-21	1.000	326.5	1.24e-21	1.000	327.0	1.20e-21	1.000	327.5	1.04e-21	1.000	328.0	9.51e-22	1.000
328.5	8.44e-22	1.000	329.0	7.26e-22	1.000	329.5	6.70e-22	1.000	330.0	6.08e-22	1.000	330.5	5.15e-22	1.000
331.0	4.56e-22	1.000	331.5	4.13e-22	1.000	332.0	3.56e-22	1.000	332.5	3.30e-22	1.000	333.0	2.97e-22	1.000
333.5	2.67e-22	1.000	334.0	2.46e-22	1.000	334.5	2.21e-22	1.000	335.0	1.93e-22	1.000	335.5	1.56e-22	1.000
336.0	1.47e-22	1.000	336.5	1.37e-22	1.000	337.0	1.27e-22	1.000	337.5	1.19e-22	1.000	338.0	1.09e-22	1.000
338.5	1.01e-22	1.000	339.0	9.09e-23	1.000	339.5	8.22e-23	1.000	340.0	7.66e-23	1.000	340.5	7.43e-23	1.000
341.0	6.83e-23	1.000	341.5	6.72e-23	1.000	342.0	6.04e-23	1.000	342.5	4.78e-23	1.000	343.0	0.00e+00	1.000
COOH														
210.0	3.12e-19	1.000	215.0	2.09e-19	1.000	220.0	1.54e-19	1.000	225.0	1.22e-19	1.000	230.0	9.62e-20	1.000
235.0	7.61e-20	1.000	240.0	6.05e-20	1.000	245.0	4.88e-20	1.000	250.0	3.98e-20	1.000	255.0	3.23e-20	1.000
260.0	2.56e-20	1.000	265.0	2.11e-20	1.000	270.0	1.70e-20	1.000	275.0	1.39e-20	1.000	280.0	1.09e-20	1.000
285.0	8.63e-21	1.000	290.0	6.91e-21	1.000	295.0	5.51e-21	1.000	300.0	4.13e-21	1.000	305.0	3.13e-21	1.000
310.0	2.39e-21	1.000	315.0	1.82e-21	1.000	320.0	1.37e-21	1.000	325.0	1.05e-21	1.000	330.0	7.90e-22	1.000
335.0	6.10e-22	1.000	340.0	4.70e-22	1.000	345.0	3.50e-22	1.000	350.0	2.70e-22	1.000	355.0	2.10e-22	1.000
360.0	1.60e-22	1.000	365.0	1.20e-22	1.000	370.0	0.00e+00	1.000						
GLY_R														
230.0	2.87e-21	1.000	235.0	2.87e-21	1.000	240.0	4.30e-21	1.000	245.0	5.73e-21	1.000	250.0	8.60e-21	1.000
255.0	1.15e-20	1.000	260.0	1.43e-20	1.000	265.0	1.86e-20	1.000	270.0	2.29e-20	1.000	275.0	2.58e-20	1.000
280.0	2.87e-20	1.000	285.0	3.30e-20	1.000	290.0	3.15e-20	1.000	295.0	3.30e-20	1.000	300.0	3.58e-20	1.000
305.0	2.72e-20	1.000	310.0	2.72e-20	1.000	312.5	2.87e-20	1.000	315.0	2.29e-20	1.000	320.0	1.43e-20	1.000
325.0	1.15e-20	1.000	327.5	1.43e-20	1.000	330.0	1.15e-20	1.000	335.0	2.87e-21	1.000	340.0	0.00e+00	1.000
345.0	0.00e+00	1.000	350.0	0.00e+00	1.000	355.0	0.00e+00	1.000	360.0	2.29e-21	1.000	365.0	2.87e-21	1.000
370.0	8.03e-21	1.000	375.0	1.00e-20	1.000	380.0	1.72e-20	0.972	382.0	1.58e-20	0.855	384.0	1.49e-20	0.737
386.0	1.49e-20	0.619	388.0	2.87e-20	0.502	390.0	3.15e-20	0.384	391.0	3.24e-20	0.326	392.0	3.04e-20	0.267
393.0	2.23e-20	0.208	394.0	2.63e-20	0.149	395.0	3.04e-20	0.090	396.0	2.63e-20	0.032	397.0	2.43e-20	0.000
398.0	3.24e-20	0.000	399.0	3.04e-20	0.000	400.0	2.84e-20	0.000	401.0	3.24e-20	0.000	402.0	4.46e-20	0.000
403.0	5.27e-20	0.000	404.0	4.26e-20	0.000	405.0	3.04e-20	0.000	406.0	3.04e-20	0.000	407.0	2.84e-20	0.000
408.0	2.43e-20	0.000	409.0	2.84e-20	0.000	410.0	6.08e-20	0.000	411.0	5.07e-20	0.000	411.5	6.08e-20	0.000
412.0	4.86e-20	0.000	413.0	8.31e-20	0.000	413.5	6.48e-20	0.000	414.0	7.50e-20	0.000	414.5	8.11e-20	0.000
415.0	8.11e-20	0.000	415.5	6.89e-20	0.000	416.0	4.26e-20	0.000	417.0	4.86e-20	0.000	418.0	5.88e-20	0.000
GLY_ABS														
230.0	2.87e-21	1.000	235.0	2.87e-21	1.000	240.0	4.30e-21	1.000	245.0	5.73e-21	1.000	250.0	8.60e-21	1.000
255.0	1.15e-20	1.000	260.0	1.43e-20	1.000	265.0	1.86e-20	1.000	270.0	2.29e-20	1.000	275.0	2.58e-20	1.000
280.0	2.87e-20	1.000	285.0	3.30e-20	1.000	290.0	3.15e-20	1.000	295.0	3.30e-20	1.000	300.0	3.58e-20	1.000
305.0	2.72e-20	1.000	310.0	2.72e-20	1.000	312.5	2.87e-20	1.000	315.0	2.29e-20	1.000	320.0	1.43e-20	1.000
325.0	1.15e-20	1.000	327.5	1.43e-20	1.000	330.0	1.15e-20	1.000	335.0	2.87e-21	1.000	340.0	0.00e+00	1.000
355.0	0.00e+00	1.000	360.0	2.29e-21	1.000	365.0	2.87e-21	1.000	370.0	8.03e-21	1.000	375.0	1.00e-20	1.000
380.0	1.72e-20	1.000	382.0	1.58e-20	1.000	384.0	1.49e-20	1.000	386.0	1.49e-20	1.000	388.0	2.87e-20	1.000
390.0	3.15e-20	1.000	391.0	3.24e-20	1.000	392.0	3.04e-20	1.000	393.0	2.23e-20	1.000	394.0	2.63e-20	1.000
395.0	3.04e-20	1.000	396.0	2.63e-20	1.000	397.0	2.43e-20	1.000	398.0	3.24e-20	1.000	399.0	3.04e-20	1.000
400.0	2.84e-20	1.000	401.0	3.24e-20	1.000	402.0	4.46e-20	1.000	403.0	5.27e-20	1.000	404.0	4.26e-20	1.000
405.0	3.04e-20	1.000	406.0	3.04e-20	1.000	407.0	2.84e-20	1.000	408.0	2.43e-20	1.000	409.0	2.84e-20	1.000
410.0	6.08e-20	1.000	411.0	5.07e-20	1.000	411.5	6.08e-20	1.000	412.0	4.86e-20	1.000	413.0	8.31e-20	1.000
413.5	6.48e-20	1.000	414.0	7.50e-20	1.000	414.5	8.11e-20	1.000	415.0	8.11e-20	1.000	415.5	6.89e-20	1.000
416.0	4.26e-20	1.000	417.0	4.86e-20	1.000	418.0	5.88e-20	1.000	419.0	6.69e-20	1.000	420.0	3.85e-20	1.000
421.0	5.67e-20	1.000	421.5	4.46e-20	1.000	422.0	5.27e-20	1.000	422.5	1.05e-19	1.000	423.0	8.51e-20	1.000
424.0	6.08e-20	1.000	425.0	7.29e-20	1.000	426.0	1.18e-19	1.000	426.5	1.30e-19	1.000	427.0	1.07e-19	1.000
428.0	1.66e-19	1.000	429.0	4.05e-20	1.000	430.0	5.07e-20	1.000	431.0	4.86e-20	1.000	432.0	4.05e-20	1.000
433.0	3.65e-20	1.000	434.0	4.05e-20	1.000	434.5	6.08e-20	1.000	435.0	5.07e-20	1.000	436.0	8.11e-20	1.000



Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
436.5	1.13e-19	1.000	437.0	5.27e-20	1.000	438.0	1.01e-19	1.000	438.5	1.38e-19	1.000	439.0	7.70e-20	1.000
440.0	2.47e-19	1.000	441.0	8.11e-20	1.000	442.0	6.08e-20	1.000	443.0	7.50e-20	1.000	444.0	9.32e-20	1.000
445.0	1.13e-19	1.000	446.0	5.27e-20	1.000	447.0	2.43e-20	1.000	448.0	2.84e-20	1.000	449.0	3.85e-20	1.000
450.0	6.08e-20	1.000	451.0	1.09e-19	1.000	451.5	9.32e-20	1.000	452.0	1.22e-19	1.000	453.0	2.39e-19	1.000
454.0	1.70e-19	1.000	455.0	3.40e-19	1.000	455.5	4.05e-19	1.000	456.0	1.01e-19	1.000	457.0	1.62e-20	1.000
458.0	1.22e-20	1.000	458.5	1.42e-20	1.000	459.0	4.05e-21	1.000	460.0	4.05e-21	1.000	460.5	6.08e-21	1.000
461.0	2.03e-21	1.000	462.0	0.00e+00	1.000									
MGLY_ADJ														
219.0	9.84e-21	1.000	219.5	1.04e-20	1.000	220.0	1.06e-20	1.000	220.5	1.11e-20	1.000	221.0	1.15e-20	1.000
221.5	1.18e-20	1.000	222.0	1.22e-20	1.000	222.5	1.24e-20	1.000	223.0	1.26e-20	1.000	223.5	1.26e-20	1.000
224.0	1.25e-20	1.000	224.5	1.24e-20	1.000	225.0	1.25e-20	1.000	225.5	1.27e-20	1.000	226.0	1.27e-20	1.000
226.5	1.29e-20	1.000	227.0	1.31e-20	1.000	227.5	1.32e-20	1.000	228.0	1.35e-20	1.000	228.5	1.37e-20	1.000
229.0	1.40e-20	1.000	229.5	1.42e-20	1.000	230.0	1.48e-20	1.000	230.5	1.53e-20	1.000	231.0	1.57e-20	1.000
231.5	1.59e-20	1.000	232.0	1.61e-20	1.000	232.5	1.62e-20	1.000	233.0	1.61e-20	1.000	233.5	1.68e-20	1.000
234.0	1.74e-20	1.000	234.5	1.80e-20	1.000	235.0	1.84e-20	1.000	235.5	1.87e-20	1.000	236.0	1.89e-20	1.000
236.5	1.91e-20	1.000	237.0	1.93e-20	1.000	237.5	1.94e-20	1.000	238.0	1.96e-20	1.000	238.5	1.96e-20	1.000
239.0	2.01e-20	1.000	239.5	2.04e-20	1.000	240.0	2.08e-20	1.000	240.5	2.10e-20	1.000	241.0	2.14e-20	1.000
241.5	2.16e-20	1.000	242.0	2.19e-20	1.000	242.5	2.20e-20	1.000	243.0	2.23e-20	1.000	243.5	2.26e-20	1.000
244.0	2.28e-20	1.000	244.5	2.29e-20	1.000	245.0	2.30e-20	1.000	245.5	2.32e-20	1.000	246.0	2.33e-20	1.000
246.5	2.35e-20	1.000	247.0	2.38e-20	1.000	247.5	2.41e-20	1.000	248.0	2.46e-20	1.000	248.5	2.51e-20	1.000
249.0	2.57e-20	1.000	249.5	2.61e-20	1.000	250.0	2.65e-20	1.000	250.5	2.67e-20	1.000	251.0	2.69e-20	1.000
251.5	2.69e-20	1.000	252.0	2.71e-20	1.000	252.5	2.72e-20	1.000	253.0	2.73e-20	1.000	253.5	2.74e-20	1.000
254.0	2.76e-20	1.000	254.5	2.78e-20	1.000	255.0	2.82e-20	1.000	255.5	2.87e-20	1.000	256.0	2.93e-20	1.000
256.5	2.98e-20	1.000	257.0	3.07e-20	1.000	257.5	3.12e-20	1.000	258.0	3.17e-20	1.000	258.5	3.21e-20	1.000
259.0	3.26e-20	1.000	259.5	3.28e-20	1.000	260.0	3.29e-20	1.000	260.5	3.31e-20	1.000	261.0	3.33e-20	1.000
261.5	3.34e-20	1.000	262.0	3.36e-20	1.000	262.5	3.38e-20	1.000	263.0	3.42e-20	1.000	263.5	3.44e-20	1.000
264.0	3.48e-20	1.000	264.5	3.54e-20	1.000	265.0	3.59e-20	1.000	265.5	3.65e-20	1.000	266.0	3.73e-20	1.000
266.5	3.80e-20	1.000	267.0	3.87e-20	1.000	267.5	3.95e-20	1.000	268.0	4.02e-20	1.000	268.5	4.08e-20	1.000
269.0	4.13e-20	1.000	269.5	4.17e-20	1.000	270.0	4.20e-20	1.000	270.5	4.22e-20	1.000	271.0	4.22e-20	1.000
271.5	4.22e-20	1.000	272.0	4.23e-20	1.000	272.5	4.24e-20	1.000	273.0	4.27e-20	1.000	273.5	4.29e-20	1.000
274.0	4.31e-20	1.000	274.5	4.33e-20	1.000	275.0	4.37e-20	1.000	275.5	4.42e-20	1.000	276.0	4.48e-20	1.000
276.5	4.56e-20	1.000	277.0	4.64e-20	1.000	277.5	4.71e-20	1.000	278.0	4.78e-20	1.000	278.5	4.83e-20	1.000
279.0	4.87e-20	1.000	279.5	4.90e-20	1.000	280.0	4.92e-20	1.000	280.5	4.93e-20	1.000	281.0	4.94e-20	1.000
281.5	4.92e-20	1.000	282.0	4.90e-20	1.000	282.5	4.86e-20	1.000	283.0	4.83e-20	1.000	283.5	4.79e-20	1.000
284.0	4.76e-20	1.000	284.5	4.72e-20	1.000	285.0	4.70e-20	1.000	285.5	4.68e-20	1.000	286.0	4.66e-20	1.000
286.5	4.65e-20	1.000	287.0	4.65e-20	1.000	287.5	4.68e-20	1.000	288.0	4.73e-20	1.000	288.5	4.78e-20	1.000
289.0	4.84e-20	1.000	289.5	4.89e-20	1.000	290.0	4.92e-20	1.000	290.5	4.92e-20	1.000	291.0	4.90e-20	1.000
291.5	4.86e-20	1.000	292.0	4.81e-20	1.000	292.5	4.75e-20	1.000	293.0	4.70e-20	1.000	293.5	4.65e-20	1.000
294.0	4.58e-20	1.000	294.5	4.48e-20	1.000	295.0	4.38e-20	1.000	295.5	4.27e-20	1.000	296.0	4.17e-20	1.000
296.5	4.07e-20	1.000	297.0	3.99e-20	1.000	297.5	3.94e-20	1.000	298.0	3.88e-20	1.000	298.5	3.82e-20	1.000
299.0	3.76e-20	1.000	299.5	3.72e-20	1.000	300.0	3.69e-20	1.000	300.5	3.68e-20	1.000	301.0	3.70e-20	1.000
301.5	3.72e-20	1.000	302.0	3.74e-20	1.000	302.5	3.74e-20	1.000	303.0	3.75e-20	1.000	303.5	3.71e-20	1.000
304.0	3.62e-20	1.000	304.5	3.51e-20	1.000	305.0	3.38e-20	1.000	305.5	3.25e-20	1.000	306.0	3.15e-20	1.000
306.5	3.04e-20	1.000	307.0	2.92e-20	1.000	307.5	2.80e-20	1.000	308.0	2.71e-20	1.000	308.5	2.63e-20	1.000
309.0	2.52e-20	1.000	309.5	2.43e-20	1.000	310.0	2.34e-20	1.000	310.5	2.25e-20	1.000	311.0	2.19e-20	1.000
311.5	2.12e-20	1.000	312.0	2.06e-20	1.000	312.5	2.02e-20	1.000	313.0	1.96e-20	1.000	313.5	1.92e-20	1.000
314.0	1.91e-20	1.000	314.5	1.88e-20	1.000	315.0	1.86e-20	1.000	315.5	1.85e-20	1.000	316.0	1.86e-20	1.000
316.5	1.87e-20	1.000	317.0	1.87e-20	1.000	317.5	1.87e-20	1.000	318.0	1.83e-20	1.000	318.5	1.75e-20	1.000
319.0	1.69e-20	1.000	319.5	1.60e-20	1.000	320.0	1.50e-20	1.000	320.5	1.41e-20	1.000	321.0	1.34e-20	1.000
321.5	1.27e-20	1.000	322.0	1.21e-20	1.000	322.5	1.18e-20	1.000	323.0	1.14e-20	1.000	323.5	1.08e-20	1.000
324.0	1.01e-20	1.000	324.5	9.62e-21	1.000	325.0	9.28e-21	1.000	325.5	8.75e-21	1.000	326.0	8.49e-21	1.000

Table 48 (continued)

WL (nm)	Abs (cm <sup>-2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>-2</sup> )	QY	WL (nm)	Abs (cm <sup>-2</sup> )	QY	WL (nm)	Abs (cm <sup>-2</sup> )	QY	WL (nm)	Abs (cm <sup>-2</sup> )	QY
326.5	8.21e-21	1.000	327.0	7.71e-21	1.000	327.5	7.38e-21	1.000	328.0	7.18e-21	1.000	328.5	6.86e-21	1.000
329.0	6.71e-21	1.000	329.5	6.63e-21	1.000	330.0	6.46e-21	1.000	330.5	6.29e-21	1.000	331.0	6.21e-21	1.000
331.5	6.18e-21	1.000	332.0	6.20e-21	1.000	332.5	5.49e-21	1.000	333.0	5.21e-21	1.000	333.5	5.38e-21	1.000
334.0	5.35e-21	1.000	334.5	5.04e-21	1.000	335.0	4.94e-21	1.000	335.5	4.90e-21	1.000	336.0	4.52e-21	1.000
336.5	4.26e-21	1.000	337.0	4.11e-21	1.000	337.5	3.76e-21	1.000	338.0	3.61e-21	1.000	338.5	3.58e-21	1.000
339.0	3.47e-21	1.000	339.5	3.32e-21	1.000	340.0	3.22e-21	1.000	340.5	3.10e-21	1.000	341.0	3.00e-21	1.000
341.5	2.94e-21	1.000	342.0	2.89e-21	1.000	342.5	2.86e-21	1.000	343.0	2.88e-21	1.000	343.5	2.88e-21	1.000
344.0	2.89e-21	0.992	344.5	2.91e-21	0.984	345.0	2.95e-21	0.976	345.5	3.00e-21	0.968	346.0	3.08e-21	0.960
346.5	3.18e-21	0.953	347.0	3.25e-21	0.945	347.5	3.30e-21	0.937	348.0	3.39e-21	0.929	348.5	3.51e-21	0.921
349.0	3.63e-21	0.913	349.5	3.73e-21	0.905	350.0	3.85e-21	0.897	350.5	3.99e-21	0.889	351.0	4.27e-21	0.881
351.5	4.47e-21	0.873	352.0	4.63e-21	0.865	352.5	4.78e-21	0.858	353.0	4.92e-21	0.850	353.5	5.07e-21	0.842
354.0	5.23e-21	0.834	354.5	5.39e-21	0.826	355.0	5.56e-21	0.818	355.5	5.77e-21	0.810	356.0	5.97e-21	0.802
356.5	6.15e-21	0.794	357.0	6.35e-21	0.786	357.5	6.56e-21	0.778	358.0	6.76e-21	0.770	358.5	6.95e-21	0.763
359.0	7.20e-21	0.755	359.5	7.44e-21	0.747	360.0	7.64e-21	0.739	360.5	7.89e-21	0.731	361.0	8.15e-21	0.723
361.5	8.43e-21	0.715	362.0	8.71e-21	0.707	362.5	9.02e-21	0.699	363.0	9.33e-21	0.691	363.5	9.65e-21	0.683
364.0	1.00e-20	0.675	364.5	1.04e-20	0.668	365.0	1.08e-20	0.660	365.5	1.11e-20	0.652	366.0	1.15e-20	0.644
366.5	1.19e-20	0.636	367.0	1.23e-20	0.628	367.5	1.27e-20	0.620	368.0	1.31e-20	0.612	368.5	1.35e-20	0.604
369.0	1.40e-20	0.596	369.5	1.44e-20	0.588	370.0	1.47e-20	0.580	370.5	1.51e-20	0.573	371.0	1.55e-20	0.565
371.5	1.59e-20	0.557	372.0	1.64e-20	0.549	372.5	1.70e-20	0.541	373.0	1.73e-20	0.533	373.5	1.77e-20	0.525
374.0	1.81e-20	0.517	374.5	1.86e-20	0.509	375.0	1.90e-20	0.501	375.5	1.96e-20	0.493	376.0	2.02e-20	0.486
376.5	2.06e-20	0.478	377.0	2.10e-20	0.470	377.5	2.14e-20	0.462	378.0	2.18e-20	0.454	378.5	2.24e-20	0.446
379.0	2.30e-20	0.438	379.5	2.37e-20	0.430	380.0	2.42e-20	0.422	380.5	2.47e-20	0.414	381.0	2.54e-20	0.406
381.5	2.62e-20	0.398	382.0	2.69e-20	0.391	382.5	2.79e-20	0.383	383.0	2.88e-20	0.375	383.5	2.96e-20	0.367
384.0	3.02e-20	0.359	384.5	3.10e-20	0.351	385.0	3.20e-20	0.343	385.5	3.29e-20	0.335	386.0	3.39e-20	0.327
386.5	3.51e-20	0.319	387.0	3.62e-20	0.311	387.5	3.69e-20	0.303	388.0	3.70e-20	0.296	388.5	3.77e-20	0.288
389.0	3.88e-20	0.280	389.5	3.97e-20	0.272	390.0	4.03e-20	0.264	390.5	4.12e-20	0.256	391.0	4.22e-20	0.248
391.5	4.29e-20	0.240	392.0	4.30e-20	0.232	392.5	4.38e-20	0.224	393.0	4.47e-20	0.216	393.5	4.55e-20	0.208
394.0	4.56e-20	0.201	394.5	4.59e-20	0.193	395.0	4.67e-20	0.185	395.5	4.80e-20	0.177	396.0	4.87e-20	0.169
396.5	4.96e-20	0.161	397.0	5.08e-20	0.153	397.5	5.19e-20	0.145	398.0	5.23e-20	0.137	398.5	5.39e-20	0.129
399.0	5.46e-20	0.121	399.5	5.54e-20	0.113	400.0	5.59e-20	0.106	400.5	5.77e-20	0.098	401.0	5.91e-20	0.090
401.5	5.99e-20	0.082	402.0	6.06e-20	0.074	402.5	6.20e-20	0.066	403.0	6.35e-20	0.058	403.5	6.52e-20	0.050
404.0	6.54e-20	0.042	404.5	6.64e-20	0.034	405.0	6.93e-20	0.026	405.5	7.15e-20	0.018	406.0	7.19e-20	0.011
406.5	7.32e-20	0.003	407.0	7.58e-20	0.000	407.5	7.88e-20	0.000	408.0	7.97e-20	0.000	408.5	7.91e-20	0.000
409.0	8.11e-20	0.000	409.5	8.41e-20	0.000	410.0	8.53e-20	0.000	410.5	8.59e-20	0.000	411.0	8.60e-20	0.000
411.5	8.80e-20	0.000	412.0	9.04e-20	0.000	412.5	9.45e-20	0.000	413.0	9.34e-20	0.000	413.5	9.37e-20	0.000
414.0	9.63e-20	0.000	414.5	9.71e-20	0.000	415.0	9.70e-20	0.000	415.5	9.65e-20	0.000	416.0	9.69e-20	0.000
416.5	9.89e-20	0.000	417.0	1.00e-19	0.000	417.5	1.02e-19	0.000	418.0	1.00e-19	0.000	418.5	1.02e-19	0.000
419.0	1.01e-19	0.000	419.5	1.01e-19	0.000	420.0	1.03e-19	0.000	420.5	1.01e-19	0.000	421.0	1.04e-19	0.000
BACL_ADJ														
230.0	1.30e-20	1.000	232.5	1.46e-20	1.000	235.0	1.68e-20	1.000	237.5	1.84e-20	1.000	240.0	2.16e-20	1.000
242.5	2.49e-20	1.000	245.0	2.65e-20	1.000	247.5	2.71e-20	1.000	250.0	3.03e-20	1.000	252.5	3.46e-20	1.000
255.0	3.46e-20	1.000	257.5	3.57e-20	1.000	260.0	3.95e-20	1.000	262.5	4.17e-20	1.000	265.0	4.17e-20	1.000
267.5	4.22e-20	1.000	270.0	4.60e-20	1.000	272.5	4.54e-20	1.000	275.0	4.33e-20	1.000	277.5	4.22e-20	1.000
280.0	4.44e-20	1.000	282.5	4.33e-20	1.000	285.0	3.90e-20	1.000	287.5	3.57e-20	1.000	290.0	3.25e-20	1.000
292.5	2.92e-20	1.000	295.0	2.60e-20	1.000	297.5	2.16e-20	1.000	300.0	1.79e-20	1.000	302.5	1.73e-20	1.000
305.0	1.46e-20	1.000	307.5	1.08e-20	1.000	310.0	9.20e-21	1.000	312.5	7.03e-21	1.000	315.0	6.49e-21	1.000
317.5	5.41e-21	1.000	320.0	5.41e-21	1.000	322.5	5.41e-21	1.000	325.0	4.33e-21	1.000	327.5	3.25e-21	1.000
330.0	3.79e-21	1.000	332.5	3.79e-21	1.000	335.0	4.33e-21	1.000	337.5	4.87e-21	1.000	340.0	5.41e-21	1.000
342.5	5.95e-21	1.000	345.0	6.49e-21	1.000	347.5	7.03e-21	1.000	350.0	8.12e-21	0.995	352.5	7.57e-21	0.960
355.0	9.20e-21	0.925	357.5	9.74e-21	0.890	360.0	1.08e-20	0.855	362.5	1.19e-20	0.820	365.0	1.41e-20	0.785
367.5	1.51e-20	0.750	370.0	1.79e-20	0.715	372.5	2.00e-20	0.680	375.0	2.11e-20	0.645	377.5	2.33e-20	0.610

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
380.0	2.60e-20	0.575	382.5	2.81e-20	0.540	385.0	3.14e-20	0.505	387.5	3.46e-20	0.470	390.0	3.90e-20	0.435
392.5	4.11e-20	0.399	395.0	4.33e-20	0.364	397.5	4.38e-20	0.329	400.0	4.65e-20	0.294	402.5	4.81e-20	0.259
405.0	5.19e-20	0.224	407.5	5.84e-20	0.189	410.0	6.06e-20	0.154	412.5	6.49e-20	0.119	415.0	6.92e-20	0.084
417.5	6.87e-20	0.049	420.0	6.82e-20	0.014	422.5	6.71e-20	0.000	425.0	6.49e-20	0.000	427.5	5.95e-20	0.000
430.0	5.73e-20	0.000	432.5	6.28e-20	0.000	435.0	6.01e-20	0.000	437.5	5.84e-20	0.000	440.0	5.95e-20	0.000
442.5	6.49e-20	0.000	445.0	5.95e-20	0.000	447.5	4.98e-20	0.000	450.0	3.79e-20	0.000	452.5	2.81e-20	0.000
455.0	1.73e-20	0.000	457.5	1.08e-20	0.000	460.0	5.41e-21	0.000	462.5	3.79e-21	0.000	465.0	2.16e-21	0.000
467.5	1.08e-21	0.000	470.0	1.08e-21	0.000	472.5	0.00e+00	0.000						
BZCHO														
299.0	1.78e-19	1.000	304.0	7.40e-20	1.000	306.0	6.91e-20	1.000	309.0	6.41e-20	1.000	313.0	6.91e-20	1.000
314.0	6.91e-20	1.000	318.0	6.41e-20	1.000	325.0	8.39e-20	1.000	332.0	7.65e-20	1.000	338.0	8.88e-20	1.000
342.0	8.88e-20	1.000	346.0	7.89e-20	1.000	349.0	7.89e-20	1.000	354.0	9.13e-20	1.000	355.0	8.14e-20	1.000
364.0	5.67e-20	1.000	368.0	6.66e-20	1.000	369.0	8.39e-20	1.000	370.0	8.39e-20	1.000	372.0	3.45e-20	1.000
374.0	3.21e-20	1.000	376.0	2.47e-20	1.000	377.0	2.47e-20	1.000	380.0	3.58e-20	1.000	382.0	9.90e-21	1.000
386.0	0.00e+00	1.000												
ACROLEIN														
250.0	1.80e-21	1.000	252.0	2.05e-21	1.000	253.0	2.20e-21	1.000	254.0	2.32e-21	1.000	255.0	2.45e-21	1.000
256.0	2.56e-21	1.000	257.0	2.65e-21	1.000	258.0	2.74e-21	1.000	259.0	2.83e-21	1.000	260.0	2.98e-21	1.000
261.0	3.24e-21	1.000	262.0	3.47e-21	1.000	263.0	3.58e-21	1.000	264.0	3.93e-21	1.000	265.0	4.67e-21	1.000
266.0	5.10e-21	1.000	267.0	5.38e-21	1.000	268.0	5.73e-21	1.000	269.0	6.13e-21	1.000	270.0	6.64e-21	1.000
271.0	7.20e-21	1.000	272.0	7.77e-21	1.000	273.0	8.37e-21	1.000	274.0	8.94e-21	1.000	275.0	9.55e-21	1.000
276.0	1.04e-20	1.000	277.0	1.12e-20	1.000	278.0	1.19e-20	1.000	279.0	1.27e-20	1.000	280.0	1.27e-20	1.000
281.0	1.26e-20	1.000	282.0	1.26e-20	1.000	283.0	1.28e-20	1.000	284.0	1.33e-20	1.000	285.0	1.38e-20	1.000
286.0	1.44e-20	1.000	287.0	1.50e-20	1.000	288.0	1.57e-20	1.000	289.0	1.63e-20	1.000	290.0	1.71e-20	1.000
291.0	1.78e-20	1.000	292.0	1.86e-20	1.000	293.0	1.95e-20	1.000	294.0	2.05e-20	1.000	295.0	2.15e-20	1.000
296.0	2.26e-20	1.000	297.0	2.37e-20	1.000	298.0	2.48e-20	1.000	299.0	2.60e-20	1.000	300.0	2.73e-20	1.000
301.0	2.85e-20	1.000	302.0	2.99e-20	1.000	303.0	3.13e-20	1.000	304.0	3.27e-20	1.000	305.0	3.39e-20	1.000
306.0	3.51e-20	1.000	307.0	3.63e-20	1.000	308.0	3.77e-20	1.000	309.0	3.91e-20	1.000	310.0	4.07e-20	1.000
311.0	4.25e-20	1.000	312.0	4.39e-20	1.000	313.0	4.44e-20	1.000	314.0	4.50e-20	1.000	315.0	4.59e-20	1.000
316.0	4.75e-20	1.000	317.0	4.90e-20	1.000	318.0	5.05e-20	1.000	319.0	5.19e-20	1.000	320.0	5.31e-20	1.000
321.0	5.43e-20	1.000	322.0	5.52e-20	1.000	323.0	5.60e-20	1.000	324.0	5.67e-20	1.000	325.0	5.67e-20	1.000
326.0	5.62e-20	1.000	327.0	5.63e-20	1.000	328.0	5.71e-20	1.000	329.0	5.76e-20	1.000	330.0	5.80e-20	1.000
331.0	5.95e-20	1.000	332.0	6.23e-20	1.000	333.0	6.39e-20	1.000	334.0	6.38e-20	1.000	335.0	6.24e-20	1.000
336.0	6.01e-20	1.000	337.0	5.79e-20	1.000	338.0	5.63e-20	1.000	339.0	5.56e-20	1.000	340.0	5.52e-20	1.000
341.0	5.54e-20	1.000	342.0	5.53e-20	1.000	343.0	5.47e-20	1.000	344.0	5.41e-20	1.000	345.0	5.40e-20	1.000
346.0	5.48e-20	1.000	347.0	5.90e-20	1.000	348.0	6.08e-20	1.000	349.0	6.00e-20	1.000	350.0	5.53e-20	1.000
351.0	5.03e-20	1.000	352.0	4.50e-20	1.000	353.0	4.03e-20	1.000	354.0	3.75e-20	1.000	355.0	3.55e-20	1.000
356.0	3.45e-20	1.000	357.0	3.46e-20	1.000	358.0	3.49e-20	1.000	359.0	3.41e-20	1.000	360.0	3.23e-20	1.000
361.0	2.95e-20	1.000	362.0	2.81e-20	1.000	363.0	2.91e-20	1.000	364.0	3.25e-20	1.000	365.0	3.54e-20	1.000
366.0	3.30e-20	1.000	367.0	2.78e-20	1.000	368.0	2.15e-20	1.000	369.0	1.59e-20	1.000	370.0	1.19e-20	1.000
371.0	8.99e-21	1.000	372.0	7.22e-21	1.000	373.0	5.86e-21	1.000	374.0	4.69e-21	1.000	375.0	3.72e-21	1.000
376.0	3.57e-21	1.000	377.0	3.55e-21	1.000	378.0	2.83e-21	1.000	379.0	1.69e-21	1.000	380.0	8.29e-24	1.000
381.0	0.00e+00	1.000												

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY	WL	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
IC3ONO2														
185.0	1.79e-17	1.000	188.0	1.81e-17	1.000	190.0	1.79e-17	1.000	195.0	1.61e-17	1.000	200.0	1.26e-17	1.000
205.0	8.67e-18	1.000	210.0	4.98e-18	1.000	215.0	2.47e-18	1.000	220.0	1.17e-18	1.000	225.0	5.80e-19	1.000
230.0	3.10e-19	1.000	235.0	1.80e-19	1.000	240.0	1.10e-19	1.000	245.0	7.00e-20	1.000	250.0	5.70e-20	1.000
255.0	5.20e-20	1.000	260.0	4.90e-20	1.000	265.0	4.60e-20	1.000	270.0	4.10e-20	1.000	275.0	3.60e-20	1.000
280.0	2.90e-20	1.000	285.0	2.30e-20	1.000	290.0	1.70e-20	1.000	295.0	1.20e-20	1.000	300.0	8.10e-21	1.000
305.0	5.20e-21	1.000	310.0	3.20e-21	1.000	315.0	1.90e-21	1.000	320.0	1.10e-21	1.000	325.0	6.10e-22	1.000
330.0	3.70e-22	1.000	335.0	0.00e+00	1.000									
MGLY_ABS														
219.0	9.84e-21	1.000	219.5	1.04e-20	1.000	220.0	1.06e-20	1.000	220.5	1.11e-20	1.000	221.0	1.15e-20	1.000
221.5	1.18e-20	1.000	222.0	1.22e-20	1.000	222.5	1.24e-20	1.000	223.0	1.26e-20	1.000	223.5	1.26e-20	1.000
224.0	1.25e-20	1.000	224.5	1.24e-20	1.000	225.0	1.25e-20	1.000	225.5	1.27e-20	1.000	226.0	1.27e-20	1.000
226.5	1.29e-20	1.000	227.0	1.31e-20	1.000	227.5	1.32e-20	1.000	228.0	1.35e-20	1.000	228.5	1.37e-20	1.000
229.0	1.40e-20	1.000	229.5	1.42e-20	1.000	230.0	1.48e-20	1.000	230.5	1.53e-20	1.000	231.0	1.57e-20	1.000
231.5	1.59e-20	1.000	232.0	1.61e-20	1.000	232.5	1.62e-20	1.000	233.0	1.61e-20	1.000	233.5	1.68e-20	1.000
234.0	1.74e-20	1.000	234.5	1.80e-20	1.000	235.0	1.84e-20	1.000	235.5	1.87e-20	1.000	236.0	1.89e-20	1.000
236.5	1.91e-20	1.000	237.0	1.93e-20	1.000	237.5	1.94e-20	1.000	238.0	1.96e-20	1.000	238.5	1.96e-20	1.000
239.0	2.01e-20	1.000	239.5	2.04e-20	1.000	240.0	2.08e-20	1.000	240.5	2.10e-20	1.000	241.0	2.14e-20	1.000
241.5	2.16e-20	1.000	242.0	2.19e-20	1.000	242.5	2.20e-20	1.000	243.0	2.23e-20	1.000	243.5	2.26e-20	1.000
244.0	2.28e-20	1.000	244.5	2.29e-20	1.000	245.0	2.30e-20	1.000	245.5	2.32e-20	1.000	246.0	2.33e-20	1.000
246.5	2.35e-20	1.000	247.0	2.38e-20	1.000	247.5	2.41e-20	1.000	248.0	2.46e-20	1.000	248.5	2.51e-20	1.000
249.0	2.57e-20	1.000	249.5	2.61e-20	1.000	250.0	2.65e-20	1.000	250.5	2.67e-20	1.000	251.0	2.69e-20	1.000
251.5	2.69e-20	1.000	252.0	2.71e-20	1.000	252.5	2.72e-20	1.000	253.0	2.73e-20	1.000	253.5	2.74e-20	1.000
254.0	2.76e-20	1.000	254.5	2.78e-20	1.000	255.0	2.82e-20	1.000	255.5	2.87e-20	1.000	256.0	2.93e-20	1.000
256.5	2.98e-20	1.000	257.0	3.07e-20	1.000	257.5	3.12e-20	1.000	258.0	3.17e-20	1.000	258.5	3.21e-20	1.000
259.0	3.26e-20	1.000	259.5	3.28e-20	1.000	260.0	3.29e-20	1.000	260.5	3.31e-20	1.000	261.0	3.33e-20	1.000
261.5	3.34e-20	1.000	262.0	3.36e-20	1.000	262.5	3.38e-20	1.000	263.0	3.42e-20	1.000	263.5	3.44e-20	1.000
264.0	3.48e-20	1.000	264.5	3.54e-20	1.000	265.0	3.59e-20	1.000	265.5	3.65e-20	1.000	266.0	3.73e-20	1.000
266.5	3.80e-20	1.000	267.0	3.87e-20	1.000	267.5	3.95e-20	1.000	268.0	4.02e-20	1.000	268.5	4.08e-20	1.000
269.0	4.13e-20	1.000	269.5	4.17e-20	1.000	270.0	4.20e-20	1.000	270.5	4.22e-20	1.000	271.0	4.22e-20	1.000
271.5	4.22e-20	1.000	272.0	4.23e-20	1.000	272.5	4.24e-20	1.000	273.0	4.27e-20	1.000	273.5	4.29e-20	1.000
274.0	4.31e-20	1.000	274.5	4.33e-20	1.000	275.0	4.37e-20	1.000	275.5	4.42e-20	1.000	276.0	4.48e-20	1.000
276.5	4.56e-20	1.000	277.0	4.64e-20	1.000	277.5	4.71e-20	1.000	278.0	4.78e-20	1.000	278.5	4.83e-20	1.000
279.0	4.87e-20	1.000	279.5	4.90e-20	1.000	280.0	4.92e-20	1.000	280.5	4.93e-20	1.000	281.0	4.94e-20	1.000
281.5	4.92e-20	1.000	282.0	4.90e-20	1.000	282.5	4.86e-20	1.000	283.0	4.83e-20	1.000	283.5	4.79e-20	1.000
284.0	4.76e-20	1.000	284.5	4.72e-20	1.000	285.0	4.70e-20	1.000	285.5	4.68e-20	1.000	286.0	4.66e-20	1.000
286.5	4.65e-20	1.000	287.0	4.65e-20	1.000	287.5	4.68e-20	1.000	288.0	4.73e-20	1.000	288.5	4.78e-20	1.000
289.0	4.84e-20	1.000	289.5	4.89e-20	1.000	290.0	4.92e-20	1.000	290.5	4.92e-20	1.000	291.0	4.90e-20	1.000
291.5	4.86e-20	1.000	292.0	4.81e-20	1.000	292.5	4.75e-20	1.000	293.0	4.70e-20	1.000	293.5	4.65e-20	1.000
294.0	4.58e-20	1.000	294.5	4.48e-20	1.000	295.0	4.38e-20	1.000	295.5	4.27e-20	1.000	296.0	4.17e-20	1.000
296.5	4.07e-20	1.000	297.0	3.99e-20	1.000	297.5	3.94e-20	1.000	298.0	3.88e-20	1.000	298.5	3.82e-20	1.000
299.0	3.76e-20	1.000	299.5	3.72e-20	1.000	300.0	3.69e-20	1.000	300.5	3.68e-20	1.000	301.0	3.70e-20	1.000
301.5	3.72e-20	1.000	302.0	3.74e-20	1.000	302.5	3.74e-20	1.000	303.0	3.75e-20	1.000	303.5	3.71e-20	1.000
304.0	3.62e-20	1.000	304.5	3.51e-20	1.000	305.0	3.38e-20	1.000	305.5	3.25e-20	1.000	306.0	3.15e-20	1.000
306.5	3.04e-20	1.000	307.0	2.92e-20	1.000	307.5	2.80e-20	1.000	308.0	2.71e-20	1.000	308.5	2.63e-20	1.000
309.0	2.52e-20	1.000	309.5	2.43e-20	1.000	310.0	2.34e-20	1.000	310.5	2.25e-20	1.000	311.0	2.19e-20	1.000
311.5	2.12e-20	1.000	312.0	2.06e-20	1.000	312.5	2.02e-20	1.000	313.0	1.96e-20	1.000	313.5	1.92e-20	1.000
314.0	1.91e-20	1.000	314.5	1.88e-20	1.000	315.0	1.86e-20	1.000	315.5	1.85e-20	1.000	316.0	1.86e-20	1.000
316.5	1.87e-20	1.000	317.0	1.87e-20	1.000	317.5	1.87e-20	1.000	318.0	1.83e-20	1.000	318.5	1.75e-20	1.000
319.0	1.69e-20	1.000	319.5	1.60e-20	1.000	320.0	1.50e-20	1.000	320.5	1.41e-20	1.000	321.0	1.34e-20	1.000
321.5	1.27e-20	1.000	322.0	1.21e-20	1.000	322.5	1.18e-20	1.000	323.0	1.14e-20	1.000	323.5	1.08e-20	1.000

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
324.0	1.01e-20	1.000	324.5	9.62e-21	1.000	325.0	9.28e-21	1.000	325.5	8.75e-21	1.000	326.0	8.49e-21	1.000
326.5	8.21e-21	1.000	327.0	7.71e-21	1.000	327.5	7.38e-21	1.000	328.0	7.18e-21	1.000	328.5	6.86e-21	1.000
329.0	6.71e-21	1.000	329.5	6.63e-21	1.000	330.0	6.46e-21	1.000	330.5	6.29e-21	1.000	331.0	6.21e-21	1.000
331.5	6.18e-21	1.000	332.0	6.20e-21	1.000	332.5	5.49e-21	1.000	333.0	5.21e-21	1.000	333.5	5.38e-21	1.000
334.0	5.35e-21	1.000	334.5	5.04e-21	1.000	335.0	4.94e-21	1.000	335.5	4.90e-21	1.000	336.0	4.52e-21	1.000
336.5	4.26e-21	1.000	337.0	4.11e-21	1.000	337.5	3.76e-21	1.000	338.0	3.61e-21	1.000	338.5	3.58e-21	1.000
339.0	3.47e-21	1.000	339.5	3.32e-21	1.000	340.0	3.22e-21	1.000	340.5	3.10e-21	1.000	341.0	3.00e-21	1.000
341.5	2.94e-21	1.000	342.0	2.89e-21	1.000	342.5	2.86e-21	1.000	343.0	2.88e-21	1.000	343.5	2.88e-21	1.000
344.0	2.89e-21	1.000	344.5	2.91e-21	1.000	345.0	2.95e-21	1.000	345.5	3.00e-21	1.000	346.0	3.08e-21	1.000
346.5	3.18e-21	1.000	347.0	3.25e-21	1.000	347.5	3.30e-21	1.000	348.0	3.39e-21	1.000	348.5	3.51e-21	1.000
349.0	3.63e-21	1.000	349.5	3.73e-21	1.000	350.0	3.85e-21	1.000	350.5	3.99e-21	1.000	351.0	4.27e-21	1.000
351.5	4.47e-21	1.000	352.0	4.63e-21	1.000	352.5	4.78e-21	1.000	353.0	4.92e-21	1.000	353.5	5.07e-21	1.000
354.0	5.23e-21	1.000	354.5	5.39e-21	1.000	355.0	5.56e-21	1.000	355.5	5.77e-21	1.000	356.0	5.97e-21	1.000
356.5	6.15e-21	1.000	357.0	6.35e-21	1.000	357.5	6.56e-21	1.000	358.0	6.76e-21	1.000	358.5	6.95e-21	1.000
359.0	7.20e-21	1.000	359.5	7.44e-21	1.000	360.0	7.64e-21	1.000	360.5	7.89e-21	1.000	361.0	8.15e-21	1.000
361.5	8.43e-21	1.000	362.0	8.71e-21	1.000	362.5	9.02e-21	1.000	363.0	9.33e-21	1.000	363.5	9.65e-21	1.000
364.0	1.00e-20	1.000	364.5	1.04e-20	1.000	365.0	1.08e-20	1.000	365.5	1.11e-20	1.000	366.0	1.15e-20	1.000
366.5	1.19e-20	1.000	367.0	1.23e-20	1.000	367.5	1.27e-20	1.000	368.0	1.31e-20	1.000	368.5	1.35e-20	1.000
369.0	1.40e-20	1.000	369.5	1.44e-20	1.000	370.0	1.47e-20	1.000	370.5	1.51e-20	1.000	371.0	1.55e-20	1.000
371.5	1.59e-20	1.000	372.0	1.64e-20	1.000	372.5	1.70e-20	1.000	373.0	1.73e-20	1.000	373.5	1.77e-20	1.000
374.0	1.81e-20	1.000	374.5	1.86e-20	1.000	375.0	1.90e-20	1.000	375.5	1.96e-20	1.000	376.0	2.02e-20	1.000
376.5	2.06e-20	1.000	377.0	2.10e-20	1.000	377.5	2.14e-20	1.000	378.0	2.18e-20	1.000	378.5	2.24e-20	1.000
379.0	2.30e-20	1.000	379.5	2.37e-20	1.000	380.0	2.42e-20	1.000	380.5	2.47e-20	1.000	381.0	2.54e-20	1.000
381.5	2.62e-20	1.000	382.0	2.69e-20	1.000	382.5	2.79e-20	1.000	383.0	2.88e-20	1.000	383.5	2.96e-20	1.000
384.0	3.02e-20	1.000	384.5	3.10e-20	1.000	385.0	3.20e-20	1.000	385.5	3.29e-20	1.000	386.0	3.39e-20	1.000
386.5	3.51e-20	1.000	387.0	3.62e-20	1.000	387.5	3.69e-20	1.000	388.0	3.70e-20	1.000	388.5	3.77e-20	1.000
389.0	3.88e-20	1.000	389.5	3.97e-20	1.000	390.0	4.03e-20	1.000	390.5	4.12e-20	1.000	391.0	4.22e-20	1.000
391.5	4.29e-20	1.000	392.0	4.30e-20	1.000	392.5	4.38e-20	1.000	393.0	4.47e-20	1.000	393.5	4.55e-20	1.000
394.0	4.56e-20	1.000	394.5	4.59e-20	1.000	395.0	4.67e-20	1.000	395.5	4.80e-20	1.000	396.0	4.87e-20	1.000
396.5	4.96e-20	1.000	397.0	5.08e-20	1.000	397.5	5.19e-20	1.000	398.0	5.23e-20	1.000	398.5	5.39e-20	1.000
399.0	5.46e-20	1.000	399.5	5.54e-20	1.000	400.0	5.59e-20	1.000	400.5	5.77e-20	1.000	401.0	5.91e-20	1.000
401.5	5.99e-20	1.000	402.0	6.06e-20	1.000	402.5	6.20e-20	1.000	403.0	6.35e-20	1.000	403.5	6.52e-20	1.000
404.0	6.54e-20	1.000	404.5	6.64e-20	1.000	405.0	6.93e-20	1.000	405.5	7.15e-20	1.000	406.0	7.19e-20	1.000
406.5	7.32e-20	1.000	407.0	7.58e-20	1.000	407.5	7.88e-20	1.000	408.0	7.97e-20	1.000	408.5	7.91e-20	1.000
409.0	8.11e-20	1.000	409.5	8.41e-20	1.000	410.0	8.53e-20	1.000	410.5	8.59e-20	1.000	411.0	8.60e-20	1.000
411.5	8.80e-20	1.000	412.0	9.04e-20	1.000	412.5	9.45e-20	1.000	413.0	9.34e-20	1.000	413.5	9.37e-20	1.000
414.0	9.63e-20	1.000	414.5	9.71e-20	1.000	415.0	9.70e-20	1.000	415.5	9.65e-20	1.000	416.0	9.69e-20	1.000
416.5	9.89e-20	1.000	417.0	1.00e-19	1.000	417.5	1.02e-19	1.000	418.0	1.00e-19	1.000	418.5	1.02e-19	1.000
419.0	1.01e-19	1.000	419.5	1.01e-19	1.000	420.0	1.03e-19	1.000	420.5	1.01e-19	1.000	421.0	1.04e-19	1.000
421.5	1.05e-19	1.000	422.0	1.06e-19	1.000	422.5	1.04e-19	1.000	423.0	1.05e-19	1.000	423.5	1.05e-19	1.000
424.0	1.01e-19	1.000	424.5	1.01e-19	1.000	425.0	1.05e-19	1.000	425.5	1.03e-19	1.000	426.0	1.02e-19	1.000
426.5	1.01e-19	1.000	427.0	9.77e-20	1.000	427.5	9.81e-20	1.000	428.0	1.00e-19	1.000	428.5	1.02e-19	1.000
429.0	9.89e-20	1.000	429.5	9.85e-20	1.000	430.0	1.04e-19	1.000	430.5	1.08e-19	1.000	431.0	1.05e-19	1.000
431.5	1.02e-19	1.000	432.0	9.64e-20	1.000	432.5	1.01e-19	1.000	433.0	1.06e-19	1.000	433.5	1.09e-19	1.000
434.0	1.04e-19	1.000	434.5	1.03e-19	1.000	435.0	1.07e-19	1.000	435.5	1.16e-19	1.000	436.0	1.09e-19	1.000
436.5	1.11e-19	1.000	437.0	9.81e-20	1.000	437.5	9.71e-20	1.000	438.0	1.06e-19	1.000	438.5	1.16e-19	1.000
439.0	1.08e-19	1.000	439.5	1.05e-19	1.000	440.0	9.70e-20	1.000	440.5	1.01e-19	1.000	441.0	1.04e-19	1.000
441.5	1.07e-19	1.000	442.0	1.02e-19	1.000	442.5	9.68e-20	1.000	443.0	1.00e-19	1.000	443.5	1.14e-19	1.000
444.0	1.13e-19	1.000	444.5	1.03e-19	1.000	445.0	9.74e-20	1.000	445.5	8.46e-20	1.000	446.0	8.70e-20	1.000
446.5	9.97e-20	1.000	447.0	1.01e-19	1.000	447.5	9.15e-20	1.000	448.0	9.41e-20	1.000	448.5	8.99e-20	1.000
449.0	1.10e-19	1.000	449.5	9.12e-20	1.000	450.0	8.56e-20	1.000	450.5	8.28e-20	1.000	451.0	6.15e-20	1.000
451.5	5.56e-20	1.000	452.0	6.47e-20	1.000	452.5	7.27e-20	1.000	453.0	5.75e-20	1.000	453.5	5.08e-20	1.000

Table 48 (continued)

WL (nm)	Abs (cm <sup>2</sup> )	QY (nm)	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY	WL (nm)	Abs (cm <sup>2</sup> )	QY
454.0	4.38e-20	1.000	454.5	3.81e-20	1.000	455.0	3.61e-20	1.000	455.5	3.61e-20	1.000	456.0	3.13e-20	1.000
456.5	2.72e-20	1.000	457.0	2.44e-20	1.000	457.5	2.22e-20	1.000	458.0	1.82e-20	1.000	458.5	1.43e-20	1.000
459.0	1.32e-20	1.000	459.5	1.05e-20	1.000	460.0	8.95e-21	1.000	460.5	8.90e-21	1.000	461.0	7.94e-21	1.000
461.5	7.04e-21	1.000	462.0	6.46e-21	1.000	462.5	5.63e-21	1.000	463.0	4.78e-21	1.000	463.5	3.94e-21	1.000
464.0	3.26e-21	1.000	464.5	2.97e-21	1.000	465.0	2.65e-21	1.000	465.5	2.46e-21	1.000	466.0	2.27e-21	1.000
466.5	2.08e-21	1.000	467.0	1.86e-21	1.000	467.5	1.76e-21	1.000	468.0	1.60e-21	1.000	468.5	1.44e-21	1.000
469.0	1.34e-21	1.000	469.5	1.20e-21	1.000	470.0	1.07e-21	1.000	470.5	1.02e-21	1.000	471.0	9.92e-22	1.000
471.5	9.97e-22	1.000	472.0	8.87e-22	1.000	472.5	8.27e-22	1.000	473.0	7.76e-22	1.000	473.5	7.15e-22	1.000
474.0	6.71e-22	1.000	474.5	6.67e-22	1.000	475.0	6.10e-22	1.000	475.5	6.17e-22	1.000	476.0	5.54e-22	1.000
476.5	5.22e-22	1.000	477.0	5.10e-22	1.000	477.5	5.17e-22	1.000	478.0	4.80e-22	1.000	478.5	4.71e-22	1.000
479.0	4.60e-22	1.000	479.5	4.35e-22	1.000	480.0	3.90e-22	1.000	480.5	3.71e-22	1.000	481.0	3.62e-22	1.000
481.5	3.52e-22	1.000	482.0	3.05e-22	1.000	482.5	3.05e-22	1.000	483.0	2.86e-22	1.000	483.5	2.53e-22	1.000
484.0	2.75e-22	1.000	484.5	2.59e-22	1.000	485.0	2.47e-22	1.000	485.5	2.36e-22	1.000	486.0	2.12e-22	1.000
486.5	1.89e-22	1.000	487.0	1.93e-22	1.000	487.5	1.86e-22	1.000	488.0	1.82e-22	1.000	488.5	1.75e-22	1.000
489.0	1.74e-22	1.000	489.5	1.72e-22	1.000	490.0	1.66e-22	1.000	490.5	1.75e-22	1.000	491.0	1.54e-22	1.000
491.5	1.74e-22	1.000	492.0	1.63e-22	1.000	492.5	1.53e-22	1.000	493.0	1.52e-22	1.000	493.5	5.85e-23	1.000
494.0	0.00e+00	1.000												